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REFRACTORY BINARY BORIDES, (1)-(9) NA
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I. A. Introduction

The wartime and post-war search for materials for high temperature applications has provided the major stimulus for recent studies of refractory binary borides. These investigations have revealed that many of the borides possess additional unusual chemical, electrical and thermal properties which make them attractive subjects for investigations less restricted in motivation. A few examples of these properties may be of interest. The electrical and thermal conductivities of ZrB_2 and TiB_2 , for example, exceed by at least one order of magnitude those of the parent metals; the melting points of these borides are more than 1000° higher than those of the pure metals. The rare earth hexaborides include among their members some of the best thermionic emitters known. Monoborides of arsenic and phosphorus show promise as high temperature seal-conductors; higher borides of these non-metals, especially AsB_6 , are extraordinarily inert to chemical attack. The cubic form of boron nitride ("borazon") is reputedly harder than diamond; it is of interest, too, for investigations of the band structures of diamond-like compounds.

Serious recent work in this field began with the elegant series of investigations by Klessling (1) in the late 40's and 50's. His work has been continued by Aronsson, Rundquist, and others at Uppsala; in France, Bertaut and Blum have made major contributions; Samsonov and coworkers in the Soviet Union, and many workers in the United States are studying the borides. The literature of this field is impressive and is growing rapidly. Fortunately, several valuable review papers and compilations of crystal and physical data have been published within the past few years.

Probably the most comprehensive collection of crystallographic data dealing with borides is contained in Pearson's "Handbook of Lattice Spacings and Structures of Metals" (2). X-ray and related measurements of more than

seventy five boride phases are summarized and comprehensive bibliographies accompany the text. Another valuable source is Hansen's "Constitution of Binary Alloys" (3). In addition to tabulations of x-ray data and bibliographical references, this work makes available in convenient form descriptions and critical commentaries on partial equilibrium diagrams for several metal-boron systems.

"Refractory Hard Metals" by Schwarzkopf and Kieffer (4) is somewhat dated in this rapidly changing field (it was published in 1953) but it does include detailed discussions of preparative methods and the physical properties of many borides as well as related carbides, nitrides and silicides. Oschneider's recently published "Rare Earth Alloys" (5) contains a very complete and critical review of the crystal structures and the physical properties of the numerous rare earth borides. "The Constitutional Diagrams of Alloys: A Bibliography" published by the Institute of Metals (2nd ed., 1956) includes extensive listings of papers dealing with many boron-metal systems (6). Also useful are the review articles by Aronson (7). These include much material absent from prior publications as well as Tables of properties and very extensive lists of bibliographical references.

Two review articles by Samsonov (8), unfortunately not yet available in English translation, serve as valuable guides to the earlier and relatively inaccessible Russian literature. The first, published in 1956, deals with the "Chemistry of Borides" (8a); the second, published in 1959, deals with "Borides of Rare Earth Metals" (8b), a field to which Samsonov has contributed substantially.

I. B. Preparation of Borides

Industrial methods of preparation of refractory borides have been discussed in detail by Steinitz (9). Most of the borides can be prepared with varying degrees of difficulty and purity, in several ways. The reduction of metal oxides, using mixtures of carbon and boron carbide as combined reducing agents and sources of boron, has been widely used. Reduction of the desired metal oxide by other metals, including aluminum and calcium, has also been employed, although

in these cases oxide residues are mixed with the product and these may be difficult to remove. When carbon is used, no oxide residues are left in the product. Fused salt electrolysis (10) is occasionally tried, though on a relatively limited scale. These and similar methods are usually introduced primarily for industrial production at low cost.

For research purposes it is generally advisable to prepare the desired borides by the direct combination of finely divided boron and metal powders (in some cases the use of metal hydrides is more convenient). Preparations are carried out at elevated temperatures. Boron nitride crucibles (previously heated in hydrogen at about 1600°C to remove oxygen present in the B_2O_3 binder) are usually suitable; graphite crucibles may be used in some instances but carbon contamination must then be guarded against. Reactions are best carried out under purified hydrogen or in vacuum. If the starting materials are known to be free from oxygen, purified argon may be used in place of hydrogen.

For preliminary, exploratory work, arc melting on a water cooled copper block (under argon) may be utilized. In general, heating by induction is preferred because of the superior temperature control possible with this method.

I. C. Classification of Boride Structures

Boron forms binary borides with a large number of metals and non-metals; their compositions range from Me_4B through MeB_{12} to some recently reported MeB_{70} phases. These cannot be classified simply in terms of the usual chemical or metallurgical rules.

In general, higher borides are formed by "large" metal atoms; smaller metal atoms tend to form metal rich borides. Klessling (11) first commented on the striking tendency of boron atoms to form bonds with other boron atoms whenever possible. He classified the structures into four, partially overlapping, groups based primarily on the arrangement of boron atoms as follows:

- 1) borides with isolated boron atoms. These include the lower borides from Me_4B to Me_2B . As the boron content increases there is a tendency for boron atoms to form isolated pairs, e.g. in Me_3B_2 and Me_5B_3 ;
- 2) borides with boron chains (single chains in MeB and double chains in Me_3B_4);
- 3) borides with two dimensional nets of boron atoms (MeB_2 and Me_2B_5);
- 4) borides with three dimensional boron frameworks (MeB_4 , MeB_6 , MeB_{12} and MeB_{10}).

In Section II the crystal chemistry of the borides will be discussed according to this scheme, followed by a description of binary borides of non-metals. The types of borides, classified according to the positions of the parent metals in the Periodic Table, will be discussed in Section III. Electrical, magnetic and other properties will be dealt with in Section IV.

The list of bibliographical references has been compiled primarily with an eye to usefulness for the general reader. It is not intended to be complete; references to early works have been omitted in many cases; others have been omitted because their reliability was open to doubt or because their contents have been dealt with adequately elsewhere.

II. Crystal Chemistry of Borides

A. Borides with Isolated Boron Atoms:

The crystal structures of most of the compounds in this category are closely related (Table I). Aronsson and Rundqvist (11) have discussed in detail the role played by "size" factors in cementite-type structures; similar considerations apply to other types discussed here. The radius ratios, r_B/r_{Me} , in all these phases exceed by a substantial margin the value (0.414) which should be most favorable for octahedral metal environments about the boron atoms. It is pointed out that the radius ratios in these phases range from about 0.64 to 0.71 and exceed even the "ideal" values for the formation of trigonal prismatic "holes" for the boron atoms. Nevertheless, the metal atoms are generally

TABLE I: Borides with Isolated Boron Atoms

Compound	Structure Type	Crystal System	Space Group	Molecules/unit cell	Unit Cell Dimensions (in Angstroms)			c/a	Density (g.cm ⁻³)		Ref.
					a	b	c		exp.	calc.	
Mn ₄ B	orthorhombic	"	Fdd	8	14.53	7.293	4.209		6.60	6.87	1d
Cr ₄ B	"	"	"	8	14.71	7.38	4.26		---	6.24	12
Be ₄₋₅ B	---	tetragonal	P4/nm	--	3.368	---	7.050		---	---	89
Co ₃ B	Fe ₃ C	orthorhombic	Pnma	4	5.225	6.629	4.408		---	5.16	13
Ni ₃ B	"	"	"	4	5.211	6.619	4.389		6.15*	6.20	13, *111
Pt ₃ B	"	"	"	4	5.463	7.567	4.852		---	10.96	14
Re ₃ B	"	"	Cmcm	4	2.890	9.313	7.258		---	19.39	15, 16
Pd ₅ B ₂	In ₅ C ₂	monoclinic	C2/c	4	12.79	4.955	5.472		---	10.58	14
(β = 97°)											
Ru ₇ B ₃	Cr ₇ C ₃	hexagonal	P6 ₃ /mc	2	7.467		4.713	0.631	10.7	10.84	17
Rh ₇ B ₃	"	"	"	2	7.447		4.78	0.639	---	10.62	15
Re ₇ B ₃	"	"	"	2	7.504		4.68	0.631	---	10.67	15
Be ₂ B	---	cubic	Fm3m	4	4.063				---	1.89	19
Cr ₂ B	CaAl ₂	tetragonal	I4/mcm	4	5.163		4.316	0.832	---	6.53	12
Fe ₂ B	"	"	"	4	5.143		4.286	0.817	---	7.19	1d
Co ₂ B	"	"	"	4	5.109		4.249	0.832	7.0	7.34	2
Ni ₂ B	"	"	"	4	5.016		4.220	0.842	6.33	6.14	2
Mo ₂ B	"	"	"	4	4.983		4.244	0.651	6.02	6.14	1e
W ₂ B	"	"	"	4	5.543		4.735	0.854	9.1	9.31	20
Ta ₂ B	"	"	"	4	5.564		4.740	0.852	16.0	16.72	1a
Ta ₂ B	"	"	"	4	5.776		4.804	0.842	---	12.56	1c

arranged in the form of distorted triangular prisms about the boron atoms, rather than in the square anti-prismatic arrangements indicated by "size" factors.

Kiessling (1 f) has noted the close relation between the Me_3B and the Me_2B structures. The former may be considered to be derived from the latter by omitting half the boron atoms. These phases will be discussed below.

In Me_3B , Me_5B_2 and Me_7B_3 the metal atoms are arranged in approximately close packed arrays with the boron atoms in the triangular prismatic "holes". The metal atoms form slightly corrugated layers, with metal atoms at the corners of alternating triangles and squares in the layers (Fig. 1). Each metal atom has from eleven to twelve nearest metal atom neighbors; the boron atoms have six metal atom neighbors at the corners of their triangular prisms and three additional metal neighbors in triangular array about the central boron atom (Fig. 2).

In these structures the metal atoms form three-dimensional networks and the boron atoms are "interstitial". Boron to boron distances are large (i.e. 2.10A or more) for adjacent occupied sites; in none of these phases are there any effective boron to boron linkages.

Aronsson and Rundqvist (11) have also noted that the metal to boron distances in borides of transition metals of Groups VII and VIII are anomalously short. In nickel and palladium borides the average metal to boron distance is 0.07A less than the sum of the atomic radii, while in comparable borides of Groups IV to VI the average metal to boron distances exceed calculated values by about 0.03A. The reasons for these differences are obscure but the effect is real. In the series V_3B_2 , Re_3B and Pd_3B for example, the metal atoms which belong to Groups V, VI and VII respectively, have almost identical radii for coordination number 12. In all three crystals the metal atoms lie at the corners of the usual triangular prisms about the boron atoms but the average short metal to boron distances decrease from 2.28A in V_3B_2 to 2.23A in Re_3B and 2.17A in Pd_3B . The authors suggest that the factors responsible for these anomalously short boron

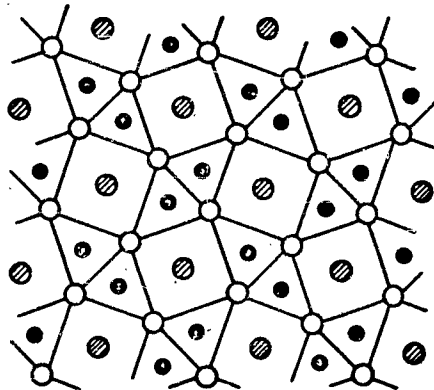


Fig. 1. Atoms in triangular and square prismatic holes.

to metal distances may also furnish an explanation of the many differences between borides of the platinum group metals and those of other transition metals.

Most of the Me_2B compounds crystallize with the $CuAl_2$ structure. In this structure sheets of tetrahedra of metal atoms form puckered layers; the metal atoms are at the corners of alternating squares and triangles within these layers (see Fig. 1). The boron atoms lie within the triangular prismatic or the square anti-prismatic holes between layers and have nine metal neighbors in the former case (as in Me_3B), and eight in the latter (i.e., at the corners of square antiprisms). The Me_4B structure may be visualized in terms of the $CuAl_2$ type, from which alternate boron atoms have been omitted. The Me_4B phases appear to have extended homogeneity ranges; possibly one limit is at the ideal formula Me_2B .

Kiessling (1.f) has noted that from a geometrical viewpoint the boron atoms may be considered to be arranged in strings within the metal lattices. Successive strings are far removed from one another (3.5 to 4.0Å) but within a given string the boron-boron distances are close to 2.10Å. These long distances apparently do not involve real boron-boron bonds, but the persistent string formations may be precursors of such bonds.

In Cr_5B_3 and the Me_3B_2 phases we note structures similar to those discussed above, except for the increasing tendency of boron atoms to link together in pairs. In V_3B_2 , for example, the boron atoms form one short (1.79Å) boron-boron bond. In these structures the isolated unit consists of a pair of boron atoms. Be_2B crystallizes in the cubic, antiperovskite structure in which no boron-boron contacts are possible ($B - B = 3.30$).

II. B. Borides with Boron Chains:

As the proportion of boron to metal atoms increases so do the possibilities for boron to boron linkages. The formation of boron pairs in V_3B_2 illustrates a trend which is continued into Me_4B_3 , MeB and beyond. For example, in the orthorhombic modification of Ni_4B_3 two-thirds of the boron atoms form infinite zig-zag chains while one-third have no close boron contacts (21).

In this structure the boron atoms are present both as isolated atoms and as chains, whereas in the monoclinic polymorph all the boron atoms participate in the formation of infinite chains.

Most of the compounds with the MeB composition belong to one of three structure types (Table II): the orthorhombic FeB type, space group $Pnma$; the orthorhombic CrB type, space group $Cmcm$; and the tetragonal MoB type, space group I_{41}^1d . Both MoB and WB crystallize in the latter form at room temperature and transform to the CrB type at elevated temperatures. The increase in crystal symmetry which usually accompanies a transformation from a low to a high temperature modification is absent here; there is actually a decrease in crystal symmetry from tetragonal to orthorhombic but this is offset in part by an approximately fifty percent reduction in cell size.

The three MeB types are closely related to one another (Fig. 2)

In all three the metal atoms are arranged at the corners of trigonal prisms.

At the centers of these prisms are boron atoms, each one bonded to six metal atoms and to two other boron atoms (in its chain).

In the Me_3B_4 compounds the metal atom arrangement is similar to that in other lower borides except for the formation of double chains of boron atoms. These may be viewed as incipient two-dimensional boron nets, precursors of the MeB_2 structures. Kiessling (1 b) had originally reported anomalously short boron-boron distances from one chain to another, but a recent careful structure analysis failed to reveal any significant differences among boron to boron bonds, either within or between chains (25).

The transition from the single boron chains of the MeB phases to the double chains of Me_3B_4 is illustrated by Ru_4B_8 , whose structure has been accurately determined by Aselius (88). Boron atoms in this crystal are of two

TABLE II: Borides with Foron Chains

Compound	Structure Type	Crystal System	Space Group	Molecules/Unit Cell	Unit Cell Dimensions (in Angstroms)			c/a	Density (g/cm ³)		Ref.
					a	b	c		exp.	calc.	
Cr ₅ B ₃	---	tetragonal	I 4/m cm	4	5.46		10.64	1.95	6.12	6.12	12
V ₂ B ₂	---	"	P 4/m cm	4	5.742		3.032	0.554	---	5.83	22
Mn ₂ B ₂	---	"	"	4	6.185		3.231	0.530	---	5.00	22
Ti ₃ B ₂	---	"	"	4	6.184		3.287	0.532	---	15.0	22
Ru ₁₁ B ₆	---	orthorhombic	Pbam	2	11.51	11.34	2.036		---	10.72	80
Hf ₄ B ₃	---	"	---	4	11.96	2.95	6.57		7.4	7.6	21
Mn ₄ B ₃	---	monoclinic	---	4	6.490	4.882	7.818		---	7.5	21
Fe ₂ B	Fe ₂	orthorhombic	Pnma	4	5.495	2.946	4.053	(a = 103.3°)	6.3	6.7	2
Mo ₂ B	"	"	"	4	5.560	2.977	4.145		6.45	6.37	1d
Co ₂ B	"	"	"	4	5.243	3.037	3.948		7.32	7.35	2
Ti ₂ B	"	"	"	4	6.12	3.06	4.56		---	---	23
VB	Cr ₂	"	Omcm	4	3.056	8.026	2.971		---	5.83	24
Cr ₂ B	"	"	"	4	2.969	7.558	2.932		6.05	6.11	1e
Mo ₂ B	"	"	"	4	3.298	8.724	3.166		---	7.56	1e
Ta ₂ B	"	"	"	4	3.276	8.669	3.157		14.0	14.23	1e
Mo ₂ B	"	"	"	4	2.925	7.396	2.986		---	7.13	2
Mo ₂ B	"	"	"	4	3.16	8.61	3.08		---	8.46	20
Mo ₂ B	"	"	"	4	3.19	8.40	3.07		14.0	15.7	96
Mo ₂ B	Mo ₂ B	tetragonal	I 4/a md	8	3.110		16.95	5.45	8.3	8.77	1a
Mo ₂ B	"	"	"	8	3.115		16.93	5.43	15.3	16.0	1a
Pt ₂ B	Anti-Mias	hexagonal	P6 ₃ /m mc	2	3.36		4.06	1.21	---	---	103
Rh ₂ B ₄	---	"	"	2	3.31		4.22	1.28	---	---	15
Ir ₂ B ₄	---	tetragonal	I 4/a md	4	2.81		10.26	3.65	---	---	15
Ta ₂ B ₄	---	orthorhombic	Lmm	2	3.29	14.0	3.13		---	13.6	1c
Mo ₂ B ₄	---	"	"	2	3.305	14.08	3.137		---	7.32	1e
Mo ₂ B ₄	---	"	"	2	3.032	12.86	2.960		---	5.92	1d
Cr ₂ B ₄	---	"	"	2	2.624	13.02	2.933		---	5.76	1b
W ₂ B ₄	---	"	"	2	3.030	13.48	2.955		---	5.46	99

types: one forms only two boron-boron linkages (i.e. single chains), the other forms three close boron bonds, two of which are involved in the formation of a bond chain, while the third serves to link two adjacent chains together.

In assessing the significance of various boron-boron or boron-metal distances often listed for these phases, it is important to bear in mind that in almost all cases the x-ray diffraction analyses yielded only metal atom positions. For the most part, boron atoms have been placed in "reasonable" positions on the basis of steric and symmetry considerations. Their locations are rarely known precisely. In many cases even the compositions of these phases are in doubt (see "Stoichiometry", Section IV).

II. C. Borides with Two-Dimensional Nets of Boron Atoms: MeB and Me_2B_2

These compounds include some of the best electric conductors, highest melting, hardest and most refractory of all the boride phases. Thirty well characterized members of this group are now known (Table III). Twenty-four are of the MeB_2 type. Their crystal structures are simple; the unit cells are hexagonal, the space group is $P6_3/m$, and there is one formula weight per unit cell. There are no variable atomic position parameters in this structure; the metal atom is at the origin of the unit cell (0,0,0) and the boron atoms lie along the long diagonal of the a' section of the unit cell at $z = 1/2$, i.e. at $1/2, 2/3, 1/2$ and $2/3, 1/3, 1/2$ (Fig. 3). The metal and the boron atoms are arranged in alternate planar hexagonal layers perpendicular to " c ". Each metal atom has six equidistant metal neighbors in its plane and twelve equidistant boron atoms, six in the layer above and six below the metal atom. Correspondingly, each boron atom has three closest boron neighbors in its plane and also forms six boron to metal bonds (Fig. 4).

The simple geometry of the unit cell facilitates calculation of interatomic distances; the boron to boron distance $= \frac{a}{\sqrt{3}}$, the metal to metal distance, within a layer perpendicular to " c ", is equal to the length of the " a " axis; the shortest metal to boron distance is $\left[\frac{a^2}{3} + \frac{c^2}{4} \right]^{1/2}$.

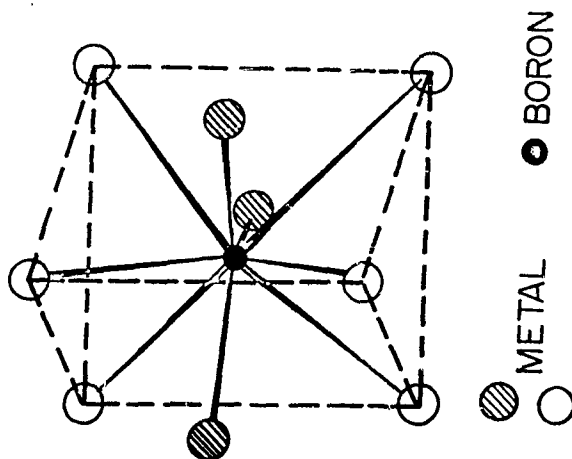


Fig. 2. Triangular prismatic environment of boron atom.

TABLE III: Borides with Two-Dimensional Boron Units

Compound	Space Group	Molecules per Unit Cell	Unit Cell Dimensions (in Angstroms)			s/a	Density (g./cm^3)		Ref.
			a	b	c		exp.	calc.	
FeB_2	P 6/m mm	1	3.03	3.52	1.14	1.42	2.07	2.63	26
AlB_2	"	1	3.09	3.20	1.04	1.04	3.17	3.16	27
ScB_2	"	1	3.14	3.51	1.10	1.10	---	3.57	28
TiB_2	"	1	3.02	3.28	1.04	1.04	4.30	4.48	2
VB_2	"	1	3.06	3.93	1.01	1.01	---	5.01	2
CrB_2	"	1	2.96	3.05	1.03	1.03	---	5.20	2
MnB_2	"	1	3.00	3.07	1.01	1.01	---	5.35	29
ZrB_2	"	1	3.29	3.63	1.16	1.16	---	5.54	5
NbB_2	"	1	3.17	3.53	1.14	1.14	6.17	6.09	2
MoB_2	"	1	3.03	3.30	1.07	1.07	6.80	6.94	2
RuB_2	"	1	3.36	3.10	1.01	1.01	---	7.77	2
ArB_2	"	1	2.62	2.55	1.01	1.01	---	10.1	33
HfB_2	"	1	3.00	3.24	1.03	1.03	---	8.5	34
TaB_2	"	1	3.14	3.47	1.05	1.05	10.5	11.2	30
TaB_2	"	1	2.86	2.41	1.05	1.05	11.7	12.6	2
OsB_2	"	1	2.67	2.57	0.97	0.97	---	17.1	35
AlB_2	"	1	3.14	3.52	1.12	1.12	---	12.1	34
SiB_2	"	1	3.31	3.34	1.19	1.19	---	7.98	33
TiB_2	"	1	3.28	3.66	1.19	1.19	---	8.34	33
NbB_2	"	1	3.25	3.63	1.17	1.17	---	8.53	35
ZrB_2	"	1	3.27	3.61	1.17	1.17	---	8.60	35
U_2B_5	"	1	3.26	3.79	1.16	1.16	---	8.69	35
U_2B_5	"	1	3.13	3.93	1.27	1.27	---	12.70	31
PuB_2	"	1	3.18	3.90	1.23	1.23	---	12.85	32
ReB_2	P 6/m mm	2	2.90	7.47	2.50	2.50	---	12.05	36
RuB_2	"	2	2.80	12.81	4.43	4.43	---	9.23	33
OsB_2	"	2	2.91	12.91	4.43	4.43	---	15.3	33
Ti_2B_5	"	2	2.98	13.67	4.65	4.65	---	13.12	1a
Ti_2B_5	"	2	2.98	13.93	4.70	4.70	---	4.62	2
La_2B_5 (short)	$\sqrt{3} \times \sqrt{3}$	3	3.01	20.93	6.45	6.45	---	7.46	1a
BaB_2	P 6/m mm	---	9.79	9.55	0.876	0.876	---	---	19

8b.

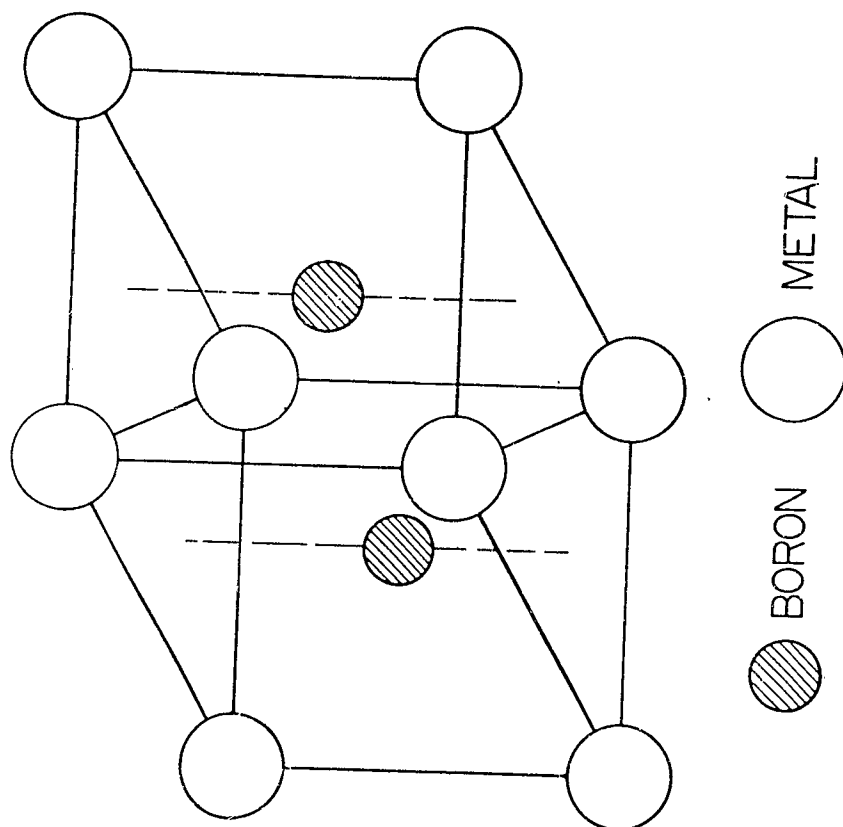
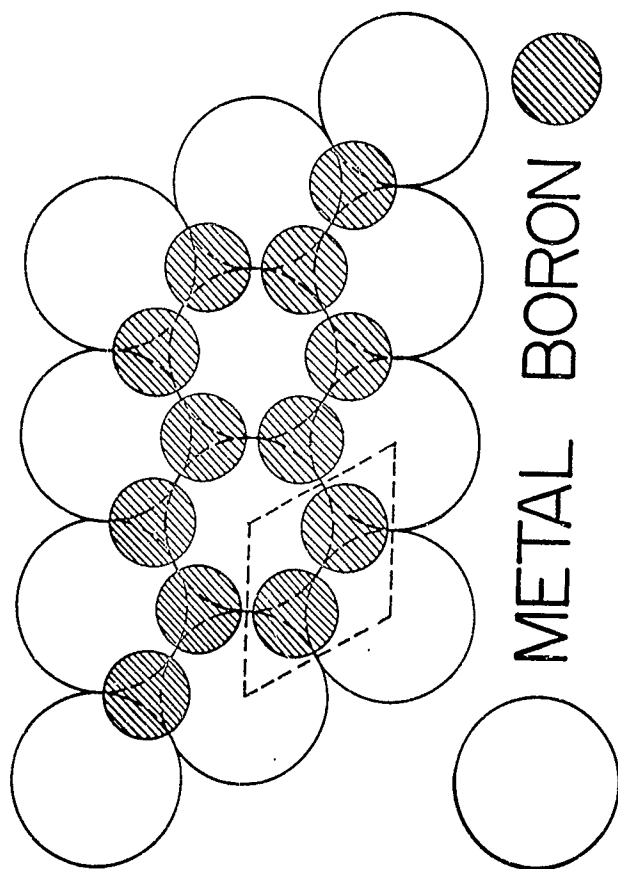


Fig. 3. Unit cell of MeB_2 .



8c.

Fig. 4. Atomic arrangement in YbB_2 projected along "c"
(one unit cell outlined by dashed lines).

Studies of numbers of compounds in which boron to boron bonds exist indicate that the "normal" boron radius is approximately 0.87 Å, i.e., the "normal" boron-boron separation is 1.74 Å (1 f). In the borides of the smaller metal atoms (e.g., Ru, Os, Mn, V, Cr, Al) the length of the "a" axis is determined primarily by such boron-boron contacts. When r_{Me} exceeds 1.53 Å, the "a" axis expands (and with it, of course, the boron-boron distance). In ZrB_2 ($r_{\text{Zr}} = 1.585$ Å) the boron-boron separation is 1.83 Å; in several recently prepared rare-earth and yttrium diborides (35) this distance exceeds 1.90 Å. Clearly, in these phases the metal atoms are in contact and their separations determine boron to boron bond lengths.

The relatively rigid "graphitic" boron layers resist both compression and extension; in the case of RuB_2 , the preservation of normal metal-metal distances in the "a" direction would lead to a boron-boron separation of only 1.53 Å. The actual boron-boron separation is 1.65 Å. Similarly, the diameter of the yttrium atom in the elementary state is 3.55 Å, and the preservation of this metal-metal separation in YB_2 would lead to a boron-boron distance of 2.05 Å; the observed distance is 1.90 Å.

The available evidence also suggests that the structure is much more tightly bonded in the "a" than in the "c" direction. The substitution of large metal atoms for smaller ones (by solid solution techniques) leads to much smaller changes in "a" than in "c" (30). The values of "a" for the 24 AlB_2 -type compounds listed in Table III range only from 2.852 to 3.298 Å. The corresponding range for "c" is 2.855 to 3.988 Å. Also, coefficients of thermal expansion are generally larger in the "c" than in the "a" direction.

Elementary considerations of the sizes of the metal atoms in MeB_2 furnish a qualitative guide to an understanding of the variation of these c/a ratios. Where the metal atoms are clearly not in contact, as in RuB_2 and OsB_2 , the c/a ratio is close to unity. The small metal atoms fit loosely within the large interstices between the boron nets and close metal-metal approaches in the "c" direction are not immeded. In the case of the larger metal atoms, the "normal" increase

in "a" is inhibited by the factors mentioned above; restrictions on lattice expansion in the "c" direction are weaker and the c/a ratio increases (up to 1.27 in UP_2).

The variation of the lattice constants of NbB_2 and TaB_2 with boron content (1 c, 31) is interesting. These phases show wide ranges of homogeneity (comparable data are not available for other diborides). Kiesel (1 c) found that $a = 3.099$ and $c = 3.224$ Å at the lower boron limit for TaB_2 (ca. 64 atomic percent boron). At the upper boron limit (ca. 72 atomic percent) $a = 3.057$ and $c = 3.291$ Å. Similar results have been reported by Brewer (31) and others (30).

For NbB_2 , Brewer found that at the lower boron limit (the exact homogeneity range was not reported) $a = 3.110$ and $c = 3.285$ Å; at the upper boron limit $a = 3.085$ and $c = 3.311$ Å. In both phases, however, the Me-B distances remain substantially constant throughout the wide composition ranges; these are 2.41 Å in TaB_2 and 2.43 Å in NbB_2 . The geometrical relation between $d(\text{Me-B})$ and the lengths of "a" and "c" show that if $d(\text{MeB})$ remains constant, an increase in "a" must be compensated for by a decrease in "c" and vice versa; this is indeed observed.

In both cases "a" decreases as the boron content of the phase increases, and increases as the boron content decreases. In MeB_2 , when the boron content is in excess of the stoichiometric 66 2/3 percent, the boron layers are filled and the metal layers are only partially full; the converse is true where boron deficiencies exist.

In these borides, the "a" dimension is determined by the balance between the "stretching" forces due to metal atoms which have diameters larger than the "normal" 3.01 Å, and strong cohesive forces within the boron network. When the boron content rises to 72 atomic percent (e.g. in TaB_2), the metal content is only 28 atomic percent and there are 8 vacancies out of every 36 available metal atom sites; this leads to a decrease in "a". Similar considerations apply to the increase in "a" when the boron content is decreased; $d(\text{Me-B})$ is constant and the observed variations in "c" simply compensate for changes in "a".

It would be of interest to make similar measurements of the variation of lattice constants (and of the Re-B distances) with stoichiometry in other suitable diborides.

Most of the diborides are very stable phases, readily formed when appropriate amounts of metal and boron powders are mixed and heated. Among the transition-metal diborides, stability tends to decrease in going from Group IV to Groups VI and VII, as well as in going from lower to higher atomic numbers within a Group. An interesting aspect of this stability trend is illustrated by the data in Table IV (30).

ReB_2 is stable above 1600°C and no WB_2 phase with the AlB_2 structure has been reported. The stable room-temperature form of these phases has the assigned formula M_2B_5 and the atomic arrangement differs substantially from that of the normal hexagonal AlB_2 type. Also, MnB_2 cannot be prepared as readily as most of the other transition-metal diborides. Kiessling (14) reported no evidence of MnB_2 in his study of the manganese-boron system but the compound was prepared subsequently by increasing the reaction temperatures to about 1500°C (29). There is evidence that the MnB_2 that is formed dissociates if cooled slowly (37).

ReB_2 crystallizes in a structure closely related to both the AlB_2 and W_2B_5 types (36). (This compound had been incorrectly assigned the formula " ReB_3 " by Aronsson, et al. (15).) The unit cell is hexagonal, the space group is $P6_3/m$ and there are two formula weights of ReB_2 per unit cell. Simple geometrical considerations illustrate that the existence of planar boron nets in ReB_2 is unlikely. In the transition-metal diborides, the boron-boron separation in the planar boron nets ranges from 1.73 to 1.81 Å. A planar arrangement of boron atoms in ReB_2 would lead to a boron-boron separation of only 1.67 Å. This arrangement, moreover, would lead to Re-B separations of only 1.87 Å. The expected minimum distance of approach is 2.24 Å ($r_B = 0.87$ Å and $r_{\text{Re}} = 1.37$ Å). These geometrical difficulties are avoided by the formation of puckered boron nets in which the boron-boron distance is 1.82 Å and the corresponding Re-B distance is 2.23 Å.

TABLE IV - Melting Points of Transition Metals and their Diborides (30).

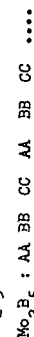
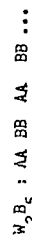
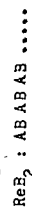
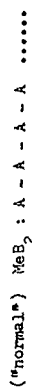
Metal	Melting Point (°C) Metal	Melting Point (°C) Diboride	M.P. Diboride M.P. Metal
Ti	1700	2920	1.62
Zr	1850	3050	1.57
Hf	2250	3240	1.40
V	1735	2400	1.33
Nb	2500	3050	1.20
Ta	2990	3200	1.06
Cr	1850	1900	1.02
Mo	2620	2100	0.83*
W	3380	2200	0.67**

* MoB_2 is stable above 1600°C .

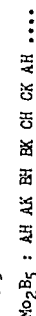
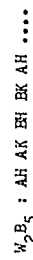
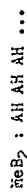
** WB_2 has not been reported. The melting point shown is that of W_2B_5 . It is possible that W_2B_5 , like Mo_2B_5 , transforms to the ReB_2 structure near the melting point.

The boron coordination around each rhenium atom consists of two trigonal bipyramids joined at a common apex with their three-fold axes collinear and parallel to the "c" axis (Fig. 5). Rhenium is at the common apex and the eight boron atoms are at the remaining vertices.

The structural relations among the closely related MeB_2 , ReB_2 , W_2B_3 and Nb_2B_3 structures are represented most clearly in terms of a notation due to Kieseling (1a). The sequence of approximately close-packed, planar, layers of metal atoms in the "c" direction is:



Kiessling denoted puckered boron sheets by K and planar sheets by H. The complete stacking sequence in the "c" direction is then:



Although the major features of the arrangement of metal and boron atoms in the Me_2B_5 phases which Klessling postulated (1.a) are probably correct, there is some doubt concerning the stoichiometry of these phases. In a detailed study of the molybdenum-boron system (20), Steinitz and co-workers could find no significant difference in boron content between Mo_2B_5 and MoB_2 . Their analyses indicated the boron contents of both phases to be slightly in excess of what was required for stoichiometric MoB_2 , but much closer to MoB_2 than to Mo_2B_5 . It is reasonable to conclude from this that " MoB_2 " is simply the high-temperature polymorph of " Mo_2B_5 " and that both phases should probably be referred to as "diborides".

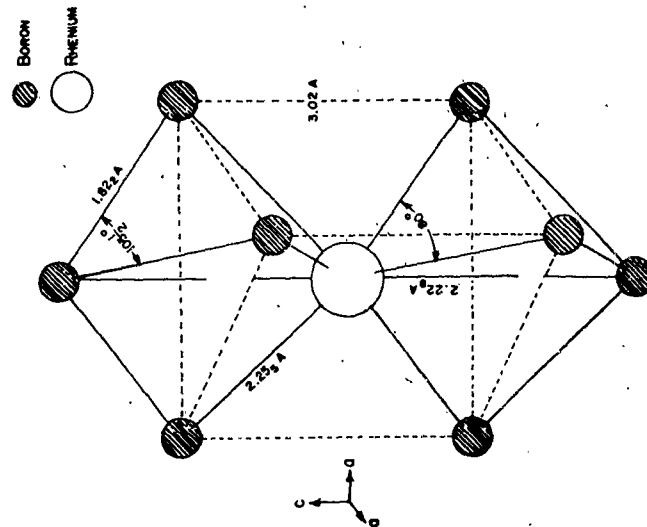


Fig. 5. Environment of rhenium atom in ReB_2 .

A study of the Os-B and Ru-B systems by Kempter and Fries (33) bears on this point. When Os was heated with two parts of boron, the major phase formed was "Os₂B₅". Heating two parts of Os with five parts of boron yielded Os₂B₅ as a minor phase together with a major unidentified phase. The assigned formulae in these cases are clearly only nominal.

A diboride of beryllium has been reported (19): the unit cell is hexagonal with $a = 9.79$ and $c = 9.55$ Å. The structure is complex and has not yet been completely analyzed.

Markovskii and Vekshina (38) have reported the preparation of diborides of Ca, Sr and Ba. No x-ray or other physical measurements were listed.

II. D. Borides with Three-Dimensional Boron Networks: MeB_4 , MeB_6 , MeB_{12} , MeB_{10} .

1. MeB_4 : The existence and the composition of UB_4 were established by Andrieux in 1929 (10). Bertaut and Rlum carried out an x-ray diffraction study of this phase (39) and reported that the unit cell is tetragonal and contains four formula weights of UB_4 ; the space group is $P4_{2/m}$ and $a = 7.066$, $c = 3.97$ Å.

These findings were confirmed by Zalkin and Templeton (40) who reported on the synthesis and crystallography of the isostructural UB_4 , ThB_4 and CeB_4 . On the basis of a single-crystal analysis of ThB_4 they determined metal atom positions and reported that there is just room for 16 boron atoms in one unit cell if the atoms were assigned reasonable radii. The latter can be arranged in the structure in only one way. The atomic arrangement, viewed in projection down the "c" axis is shown in Fig. 6.

The thorium lattice consists of planar layers as shown, each thorium having five metal atom neighbors in its own layer. Between the layers are holes bounded by six thorium atoms as in MeB_2 , i.e., with three thorium atoms "above" and three "below" the hole. There are four such holes in the unit cell and one boron atom goes into each. There are also larger holes bounded by eight thorium

atoms at the corners of a square prism; there are two such "square" holes per unit cell and an octahedron of six boron atoms fits neatly in each of them, just as in MeB_6 . These positions are clearly seen in Fig. 6.

The MeB_4 structure is thus a hybrid of MeB_2 and MeB_6 , both in terms of composition and of structure. The boron atoms in adjacent holes, of either type, are in contact and form a continuous three-dimensional network. It was not possible to locate the boron atoms directly by x-ray diffraction methods; their positions were inferred on steric grounds. The parameters were calculated by trial and error to make the B-B bonds as nearly equal in length as possible and to place the boron atoms as far from the thorium atoms as possible.

Tetraborides of most of the remaining rare-earth and related metals have since been prepared and lattice constants are shown in Table V.

Efforts to prepare EuB_4 by reactions of Eu_2O_3 with amorphous boron have been unsuccessful (41). Initial efforts to prepare LaB_4 by similar reactions were also unsuccessful and this tetraboride could only be prepared by direct reaction of metallic lanthanum with boron (41). It is possible that a similar reaction between metallic europium and boron may be made to yield EuB_4 .

Recently evidence for the formation of the isostructural CaB_4 was reported by Deane and Johnson (47).

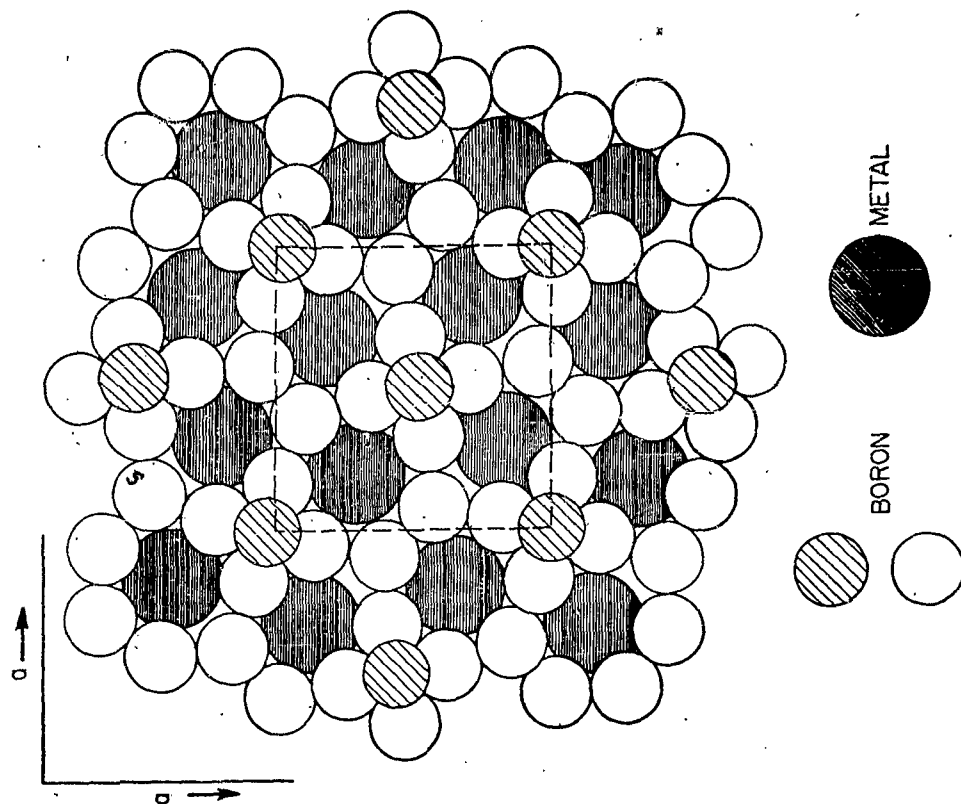
Fruchart (37) has reported that MnB_2 decomposes on slow cooling to yield Mn_3B_4 plus a second phase. The latter appears to be MnB_4 ; x-ray powder data for this phase were listed; its structure is unknown.

Chrétien and Helgorsky (46) have discussed the preparation of MoB_4 and WB_4 . These are isomorphous, crystallizing in tetragonal unit cells with $a = 6.34$ and $c = 4.50$ Å. The unit cells contain four formula weights of MeB_4 .

The MoB and W-B systems had been studied intensively by several groups previously and their failure to detect the tetraborides appears to be explained, in part, by Chrétien and Helgorsky's analysis of the thermal stability of MoB_4 and WB_4 .

TABLE V. - Tetragonal Tetraborides

Metal	Lattice Constants (Å)			Density g/cm ³	Density (calc.) g/cm ³	Ref.
	a	b	c/a			
Ca	7.11	4.11	0.576	---	2.67	47
Y	7.111	4.017	0.565	---	4.33	5
Th	7.256	4.113	0.566	---	8.45	40
U	7.075	3.979	0.562	---	9.10	40
Pa	7.10	4.014	0.565	---	9.39	32
La	7.30	4.17	0.571	---	5.44	41
Ce	7.205	4.090	0.568	---	5.72	40
Pr	7.20	4.11	0.570	---	5.71	42
Nd	7.219	4.102	0.568	---	5.64	43
Pm	---	---	---	---	---	---
Sm	7.174	4.070	0.567	---	5.12	43
Eu	---	---	---	---	---	---
Gd	7.144	4.048	0.566	---	6.44	43
Tb	7.118	4.029	0.566	---	6.60	---
Dy	7.101	4.017	0.566	---	6.74	---
Ho	7.086	4.008	0.566	---	6.86	---
Er	7.071	3.997	0.565	---	6.99	---
Tm	7.05	3.99	0.566	---	7.10	44
Yb	7.01	3.96	0.571	---	7.30	42
Lu	7.00	3.94	0.563	---	7.50	45
Yb	6.34	4.50	0.71	4.8	4.96	46
Al	6.34	4.50	0.71	6.3	6.40	46

Fig. 6. Atomic arrangement in MeB₄ (projected along c⁰).

Pure MoB_4 and WB_4 (prepared by heating the metals and boron in vacuum to 1400°C) dissociate at 1600°C to give Mo_2B_5 and MoB (and the corresponding tungsten compounds). In the presence of even small amounts of carbon, dissociation to the lower borides occurs at relatively low temperatures. It appears likely that previous investigators did not observe the tetraborides because of excessively high reaction temperatures or carbon contamination.

2. MeB_6 : All the rare-earth metals, as well as calcium, strontium, barium, thorium and plutonium form isostructural hexaborides (Table VI). The crystal structure was first determined by Stackelberg and Neumann (48). The unit cell is cubic and contains one formula weight of MeB_6 . The space group is $\text{Pn}\bar{3}\text{m}$; the metal atom is at the center of the cell with boron atoms arranged at the vertices of compact, regular octahedra, linked to one another by B-B bonds to form a three-dimensional boron network (Figs 7, 8).

The three-dimensional nature of the boron network may be emphasized by considering the structure in terms of a cube, each of whose eight corners has been truncated by planes perpendicular to the body diagonals. The planes cut the cube edges about each corner at three points; in MeB_6 a boron atom is located at each of these points. The metal atom is located at the center of the large hole within the cube (Fig. 8). Each metal atom is coordinated to 24 boron atoms; each boron atom in turn forms four boron-metal bonds and five boron-boron bonds. Four of the latter represent intra-octahedral bonds; the fifth is a link to another octahedron. Although there is only one variable position parameter in this structure (i.e., boron atoms are at $x, 0, 0$ etc.), this has not been determined with precision by x-ray diffraction methods because of the difficulties associated with the location of light atoms in the presence of heavy metal atoms. Generally the boron positions have been established by assuming that all boron-boron bonds must be equal in length. This condition is

TABLE VI: Properties of Hexaborides

Metal	Lattice Const. (in Ångströms)	Density (g. cm ⁻³)	Coefficient of Linear Thermal Expansion (°C ⁻¹)	Melting Point °C	ΔH _f Kcal/mole	Ref.
Ca	4.145 46	2.45	6.5	2235 105	---	1
Sr	4.198 46	3.42	6.7	2235 105	---	---
Ba	4.288 46	4.31	6.8	2270 105	---	---
Sc	4.435 46	2.1(1)	---	---	---	---
Y	4.413 49	3.57	6.2	2300 123	-24	123
Th	4.113 49	7.09	7.0	2195 105	---	---
Pu	4.115-4.140 32	7.28-7.13	---	---	---	---
La	4.143 42	4.72	6.4	2530 8b	---	---
Ce	4.141 49	4.79	7.3	2190 105	-51116	130
Pr	4.130 42	4.85	7.5	---	---	---
Nd	4.125 43	4.94	7.3	2540 8b	---	---
Pm	---	---	---	---	---	---
Sm	4.133 43	5.86	6.0	---	---	---
Eu	4.178 41	4.94	6.8	---	---	---
Gd	4.108 43	5.31	6.7	2100 eb	---	---
Tb	4.102 43	5.39	7.5	---	---	---
Dy	4.095 43	5.46	---	---	---	---
Ho	4.086 43	5.55	---	---	---	---
Er	4.102 41	5.58	---	---	---	---
Tm	4.110 44	5.57	---	---	---	---
Yb	4.147 43	5.54	5.8	---	---	---
Lu	4.111 49	5.73	---	---	---	---
B: Tetragonal						
Be ₂ C	Tetragonal	Space Group #4, 2, 2, 2	Z	Lattice Constants (Å)	Density (g. cm ⁻³)	Ref.
Cr ₂ C	"	"	2	10.16 11.28	2.35	19
	"	"	4	5.47 7.15	3.35	51

*This value is probably incorrect.

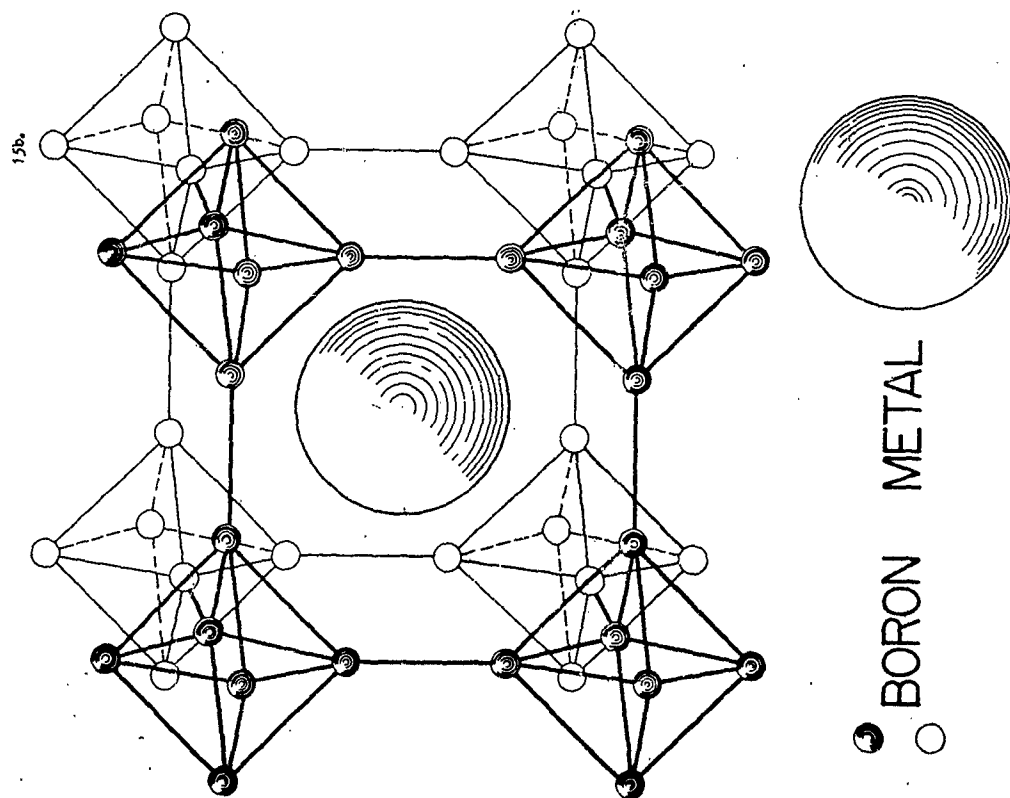


Fig. 7. Atomic arrangement in MeB_2 .

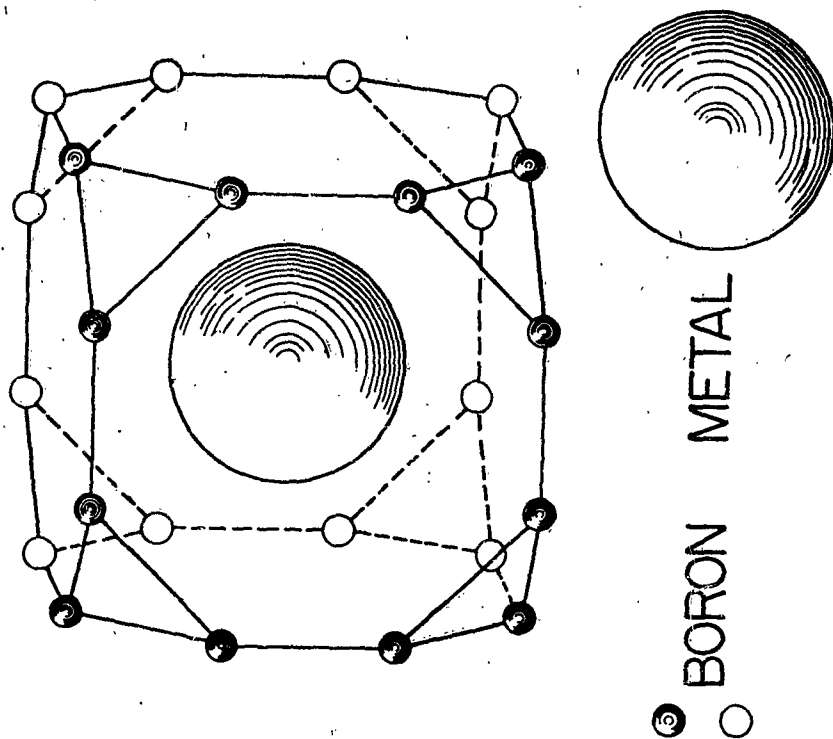


Fig. 8. Boron "cage" in MeB_6 .

satisfied by setting the variable position parameter of a boron atom at:

$$x = \frac{1}{2 + \sqrt{2}} = 0.293. \text{ Careful x-ray diffraction or neutron diffraction studies}$$

are needed to check the validity of this assumption.

The rigidity of the boron network in MeB_6 is shown by the small coefficients of thermal expansion and by the narrow range of lattice constants of these phases. Although the diameters of the metal atoms in MeB_6 range from 3.55 to 4.45 Å (for coordination number 12), the lattice constants vary only from 4.096 to 4.268 Å; the three-dimensional boron network in the hexaborides resists stretching even more than did the planes of boron atoms in the diborides.

The boron network in MeB_6 is also a remarkably open one. The smallest radius of the "interstitial" holes which serve as sites for the metal atoms equals $a/2$ and this dimension is substantially larger than the radii of any of the metals listed in Table VI with the exception of Ba. As a result, the boron-boron distance in BaB_6 is increased from the "normal" 1.74 Å to 1.77 Å. In the other MeB_6 phases it ranges from 1.70 to 1.735 Å. It would be particularly interesting to establish the boron positions in BaB_6 precisely in order to ascertain whether all B-B bonds have been stretched uniformly or whether the elongation has been confined to the interoctahedral bonds, leaving the octahedral dimensions unchanged.

A careful study of the effective atomic sizes of the rare-earth elements was carried out by Klemm and Bommer (52). They found that, on proceeding from La to Lu, these elements with the exception of Eu and Yb showed a regular decrease in atomic size. The atomic radii of the two exceptions, Eu and Yb, are about 10% above the "normal" curve for the other rare-earth elements (Fig. 9). These anomalies are associated with the abnormal valencies of these metal atoms; while most of the rare-earth metals are effectively trivalent, Eu and Yb show a large amount of divalent character. The withdrawal of one electron from the outermost orbit to fill a gap in an inner one results in the observed increased sizes of these atoms.

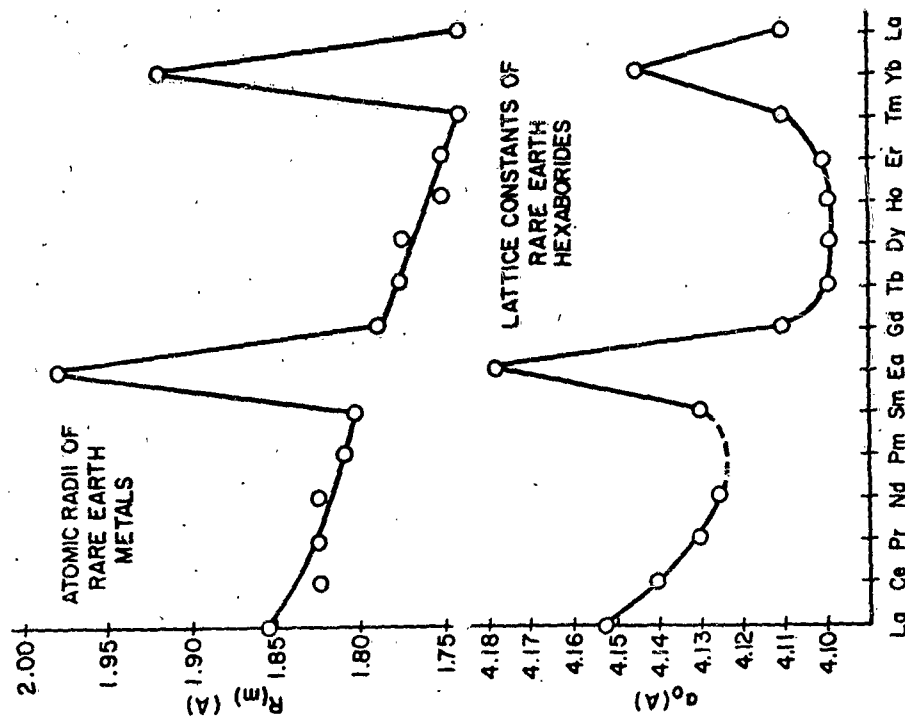


Fig. 9. Dimensions of the rare earth metals and their hexaborides.

The dimensions of the MeB_6 unit cells (Fig. 9) show a similar, though less pronounced, anomaly in the case of EuB_6 and YbB_6 . It appears, therefore, that the effective valence state of the rare-earth metals in the hexaborides is very much like that of the uncombined metals.

The sizes of the rare-earth metal ions (Me^{3+}) show no anomalies comparable to the above; these sizes decrease regularly from La^{3+} (1.061 Å) to Lu^{3+} (0.848 Å). The lattice dimensions of the various MeB_6 and MeB_{12} compounds listed in Tables V and VII also show a monotonic decrease with increasing atomic number of the metal and a distinction may therefore be drawn between the relatively "metallic" character of the MeB_6 compounds and the relatively "ionic" MeB_4 and MeB_{12} compounds.

The cubic hexaborides require, as a necessary but not sufficient condition for structural stability, that the metal atoms be "large". The smallest of the metals crystallizing in this structure, Lu, has a radius of 1.72 Å for C.N.12.

Hexaborides of relatively small metal atoms, (Mg, Be, Cr) have also been reported but these have complex structures which have not yet been solved. The dimensions of the BeB_6 phase are of some interest. These are almost identical (19) with those of AlB_{12} (53) and the tetragonal polymorph of boron reported by Talley, LaPlaca and Post (54). Intensities of lines of the BeB_6 powder pattern differ significantly from those of AlB_{12} but are not appreciably different from those of the tetragonal boron. The authors mention the possibility that BeB_6 may lie at one end of an extended homogeneity range which terminates in this tetragonal form of boron at the other end (19).

3. Metallic Dodecaborides: The first compound of this type, UB_{12} , was described by Bertaut and Blum in 1949 (39). The unit cell is cubic and contains four formula weights. The space group is $\text{Fm}\bar{3}\text{m}$. Steric considerations, plus comparisons of observed and calculated intensities, indicated to Bertaut and Blum that the one variable position parameter in the structure, that of a boron atom, was $x = \frac{1}{6}$. This leads to a highly symmetrical structure in which the metal atoms

TABLE VII: Metallic Dodecaborides

Metal	Lattice Constant (Å)	Density (g/cm ³)		d (Å)	B - B (Å)	Coef. of Thermal Exp. ($\times 10^6$)	Melting Point (°C)	Ref.
		exp.	calc.					
Tb	7.505	---	4.540	1.769	2.798	---	---	59
Dy	7.501	---	4.600	1.768	2.796	---	---	57
Ho	7.492	---	4.655	1.766	2.792	$3.0 \pm .2^*$	---	57
Er	7.484	---	4.706	1.764	2.789	$3.0 \pm .2^{**}$	---	57
Y	7.476	---	4.756	1.762	2.786	---	---	57
Yb	7.469	---	4.813	1.760	2.783	---	---	59
La	7.464	---	4.868	1.759	2.782	---	---	57
Y	7.500	---	3.444	1.763	2.796	---	---	57
Zr	7.403	3.7	3.611	1.746	2.761	---	2680	55
U	7.473	---	5.555	1.761	2.765	---	---	39

* From -150° to +200°C.

** From 30 to 350°C.

can be described as being at the centers of regular cubo-octahedra with boron atoms at each of their twenty-four vertices (Fig. 10). Each boron atom is coordinated to two metal and five boron atoms. The structure may be visualized, alternatively, in terms of a modified NaCl-type structure with the metal atoms in place of the sodium and smaller cubo-octahedral groupings of twelve boron atoms in place of the chloride ions (Fig. 11).

Subsequently the isomorphous ZrB_{12} was prepared; this phase is stable above 1600°C and could be preserved at room temperature only by quenching. Surprisingly, in spite of the close similarity between Zr and Hf, HfB_{12} could not be prepared nor could dodecaborides of the other transition metals of Groups IV, V, and VI (56).

The large coordination number of the metal atoms in the MeB_{12} structure, together with the observed restriction of its synthesis to two of the largest of the transition-metal atoms, Zr and U, indicated that a necessary condition for the formation of this phase was the presence of metal atoms with large effective radii. The experiences with the Zr and Hf preparations also suggested that the zirconium atom was near the lower limit of the permissible atomic size (the effective radii of Zr and Hf in the elementary state are 1.585 and 1.575 Å respectively).

Post, Glaser and Moskowitz (42) have described unsuccessful attempts to prepare dodecaborides of the rare-earth metals La, Ce, Pr, Sm, Cd and Yb. All of these have, in the elementary state, effective radii exceeding 1.80 Å. In all of these preparations no borides were obtained with boron content higher than that corresponding to MeB_6 . More recently these preparations were repeated using boron and oxides of La, Ce, Pr, Nd, Sm, Eu, Cd, Tb, Ho, Er, Tm, Yb, Lu, Sc and Y (57). Only Dy, Ho, Er, Tm, Lu and Y* formed dodecaborides; the others did not, in apparent agreement with previous findings (42). However, when the reaction was carried out

*Seybolt (58) reported the preparation of YB_{12} shortly before Laplace and Post.

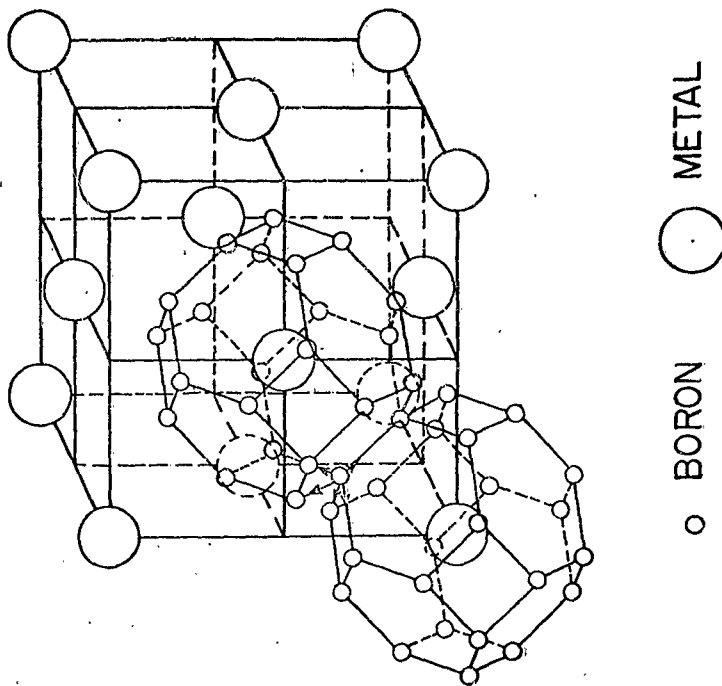


Fig. 10. Environment of metal atoms in MeB_{12} .

using powdered metal in place of the metal oxide, it was found that YbB_{12} and YbB_6 were also formed, although neither could be prepared from the oxides (59).

It is evident that the effective size of the metal atom plays a critical role in the formation of the dodecaborides. If we assume that the boron atoms are essentially spherical and that their radii are equal to half the B-B internuclear distances, then the radii of the "holes" inside the large cubo-octahedra of boron atoms about each metal range from 1.89 to 1.91 Å (Table VII). The rigid boron framework will not accommodate the larger rare-earth metal atoms whose effective radii (with twenty-four fold coordination) are appreciably greater than 1.91 Å.

The preparation of YbB_{12} is particularly interesting in this connection. It will be recalled that the unit cell of YbB_6 is anomalously large, as is the radius of the Yb atom in the elementary state, whereas the dimensions of the YbB_4 unit cell are "normal". After their initial failure to prepare YbB_{12} , Laplace, Rinder and Post (57) explained this in terms of the anomalously large size of the Yb atoms; it appeared that the effective radius of the Yb atom was larger than that of the available site in the dodecaboride lattice. It is evident that this "explanation" was premature, at least for YbB_{12} .

Chrétien and Lavéant (60) have recently reported the preparation of GaB_{12} and the indexing of the x-ray powder pattern of this phase. Seybolt (58) had previously reported that gallium does not react with boron. Efforts have been made to repeat this preparation of GaB_{12} (61). It was found the "GaB₁₂" could be formed only when the procedure used by Chrétien and Lavéant was followed closely, i.e. when the ingredients were heated in vacuum in a silica tube. No reaction occurred when aluminum or boron nitride crucibles were used. A closer analysis of the "GaB₁₂" powder pattern revealed further that it is made up entirely of lines due to H_2O and to $\text{Si}(m)$. There is no reliable indication in the x-ray pattern that a new phase has been formed.

18b.

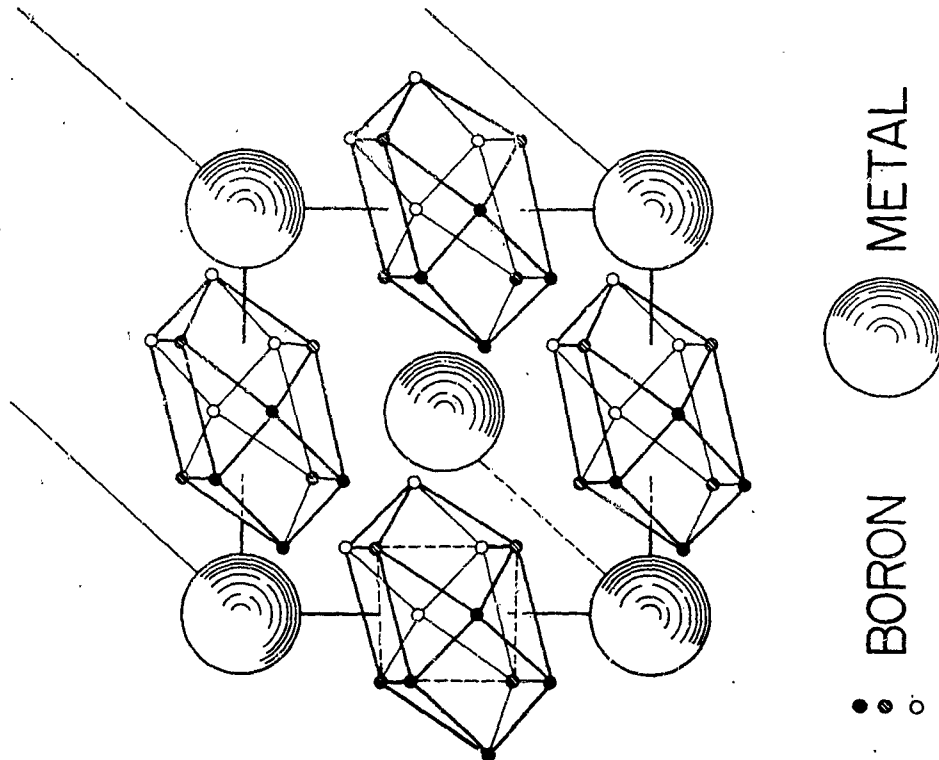
Fig. 11. Cubo-octahedra of boron atoms in LaB_{12} .

TABLE VIII: Aluminum Borides (53)

Compound	Crystal System	Space Group	Z	a	b	c	Density (gm.cm ⁻³) expt. calc.
AlB ₂	hexagonal	P 6/m mm	1	3.009		3.262	3.17 3.16
AlB ₁₀	orthorhombic	Bmm	5.2	8.88	9.10	5.69	2.54 ---
α -AlB ₁₂	tetragonal	P ₄ ² ₂ ² (?)	14.5	10.16		14.28	2.56 ---
β -AlB ₁₂	orthorhombic	Imma	16	12.34	12.63	10.16	2.60 ---
γ -AlB ₁₂	"	P2 ₁ 2 ₁ 2 ₁	29	16.6	17.5	10.2	2.56 ---

One additional group of dodecaborides should be mentioned: the AlB₁₂ compounds. Crystallographic data for these phases are listed below in Table VIII (53).

There is a striking similarity between the cell dimensions of α and β AlB₁₂ and those of the tetragonal polymorph of boron mentioned in connection with BeB₆ (54). Dimensions of the latter are a = 10.12, c = 14.14 Å but the intensities of the lines of the x-ray powder patterns of the two phases differ significantly. It is likely that these three aluminum-boride phases bear close structural relationships to one another, but no complete crystal structure determination has yet been reported.

4. Higher Borides: Seybolt (58) reported the preparation of a cubic yttrium boride with an yttrium content of from 1 to 2 atomic percent. This may be the same phase reported by Lundin (95) as YB₇₀, but the latter states that the unit cell is tetragonal with a = 11.75 and c = 12.62 Å.

LaPlaca (35) has reported the preparation of cubic borides of Ho, Tb, and Yb with compositions approximating MeB₇₀. His powder diffraction data indicate that the lattice is primitive and that the unit cell dimensions are all approximately 11.75 Å. Preliminary single-crystal analyses of "YB₇₀" by Kasper (52) reveal that the unit cell is cubic but that the true lattice constant is 23.50 Å, rather than the 11.75 Å indicated by powder data. These phases are remarkably hard and refractory; further work on them should be worth while.

II. E. Non-Metallic Borides:

1. MeB (Isolated Boron Atoms): Hexagonal boron nitride (59) is a highly refractory compound, widely used in high temperature technology. Although it is readily oxidized at 600-700°C to N₂ and B₂O₃ by such oxidizing agents as carbon dioxide, water vapor and oxygen, it is extremely stable even at much higher temperatures in the proper atmosphere. In hydrogen it may be used above 2000°C without appreciable decomposition; in nitrogen still higher temperatures are permitted (63).

The similarity between hexagonal boron nitride and the isoelectronic graphite is emphasized by the widespread use of terms like "white graphite" or "white lamblack" for boron nitride. The crystal structures of the two compounds are very similar. Unit cell dimensions, in Å, are:

	$\frac{a}{\text{Å}}$	$\frac{c}{\text{Å}}$	$\frac{c/a}{\text{Å}}$	$\frac{\text{density (g./c.c.)}}{\text{Å}^3}$
Graphite	2.464	6.736	2.73	2.26
Boron nitride	2.504	6.661	2.66	2.27

Both structures contain planar hexagonal nets of atoms perpendicular to c, separated by a distance equal to half the length of "c" in each case. In a careful investigation of the crystal structure of BN, Pease (64) demonstrated that it differs significantly from graphite. In the latter, atoms in successive layers are situated directly above the centers of hexagonal rings directly underneath; in boron nitride, hexagonal rings in successive layers are situated directly above one another, but the boron atoms in one layer are above the nitrogen atoms of the adjacent one, etc.

The similarity between boron nitride and graphite has led many investigators to speculate on the possibility of synthesizing a cubic, diamond-like boron nitride (63). This cubic modification, a typical cubic "III-V" compound, was finally synthesized by Wentorf (65) at high temperatures and pressures; the lattice constant is 3.615 Å compared with 3.567 Å for diamond.

The synthesis of the analogous cubic BP phase (cubic, zincblende structure) has been reported by three groups of investigators (66, 67, 68). The compound is prepared by direct reaction of boron and phosphorus in sealed evacuated silica tubes at about 1000°C and by reactions between BCl₃ and either AlP or phosphorus plus hydrogen (69).

The isomorphous BAs phase can also be prepared by the direct union of boron and arsenic at 800°C (68). Efforts to prepare BSB were unsuccessful. It is interesting to note that Welker and Weiss (70) had predicted that both BP and BAs would crystallize in the cubic zincblende structure. Lattice dimensions of the cubic EX phases are:

	$a_0 (\text{Å})$
BN	3.615
BP	4.538
BAs	4.777

BP and BAs decompose when heated above 1100°C; phosphorus and arsenic are lost, and higher borides, similar in structure to boron carbide and alpha boron, are formed (71). Williams and Ruehrwein (69) have discussed the decomposition of BP and BAs and the formation of these higher borides.

2. The Boron Carbide Structure Type: The crystal structure of boron carbide is well known. It was first determined by Zhdanov and Sevast'yanov (72) and confirmed shortly thereafter by Clark and Hoard (73). The unit cell is rhombohedral and contains one B₁₂C₃ structural unit. The boron atoms are situated at the vertices of compact, nearly regular, icosahedra which are linked together by B-B bonds to form a three-dimensional network. In each unit cell three carbon atoms are arranged linearly, parallel to the three-fold axis of the rhombohedral cell, in large holes formed by the approximately close-packed large boron icosahedra.

Recently Decker and Kasper (74) described the crystal structure of "alpha" boron. To a good approximation this structure may be derived from that of boron carbide by the omission of the carbon atoms from the large interstitial holes in the latter. The arrangement of boron atoms at the vertices of the icosahedra and the linking together of those icosahedra to form a three-dimensional network are essentially identical in both structures.

Other recent work also indicates that the structure type once considered to be characteristic only of boron carbide is much more common than previously supposed (71). It occurs not only in "alpha" boron but also when atoms of many different kinds are present interstitially.

For example, Matkovich (75) has reported preliminary results of an analysis of the crystal structure of B_3P_2 ; Perri, Laplace and Post (68) have reported the preparation of B_3As_2 . The unit cell of this arsenide had been indexed originally (from powder data) on the basis of a C-face centered orthorhombic unit cell. Re-examination of the powder data has shown that the pattern could be indexed equally well on the basis of the alpha boron type of rhombohedral cell, and a detailed comparison with the patterns of the phosphide and the carbide indicates that the rhombohedral indexing is correct. The ambiguity in indexing and the consequent assignment of two different crystal systems resulted from the fact that, to better than one part in 5000, the ratio $\left[\frac{d_{(001)}}{d_{(100)}} \right]^2$ was exactly 5000. As a result, different sets of indices fortuitously yielded equally good agreement between observed and calculated values of "d".

A similar ambiguity in indexing was encountered in connection with the " B_3O " phase reported by Pasternak (76) who indexed the x-ray powder data on the basis of an orthorhombic unit cell with $a = 8.20$, $b = 5.35$ and $c = 5.13$ Å. Chemical analysis had indicated that the composition was close to B_6O . This composition, however, taken in conjunction with the assumed orthorhombic unit cell, implied a calculated density which was less than the measured one. It was therefore assumed that the ideal composition of the new phase was B_7O which, together with the assumption that small amounts of B_2O_3 were present as impurities, led to satisfactory agreement between calculated and observed densities. However, just as in the case of the arsenide mentioned above, the x-ray powder pattern can be indexed more satisfactorily on the basis of a rhombohedral unit cell; the formula B_7O_2 leads to a calculated density of 2.65 compared with the observed value of 2.64 g/cc.

In B_7O as in B_3As_2 , whose pattern had also been indexed incorrectly on the basis of an orthorhombic unit cell, the ratio $\left[\frac{d_{(001)}}{d_{(100)}} \right]^2$ is exactly integral within the limits of experimental error. It is 7.00 in B_7O and 5.000 in B_3As_2 . The structural significance, if any, of these unusual relationships is not clear.

A subsequent single crystal analysis of this boron-silicon phase (81) led to a modification of the $B_{12}Si_3$ formula; the x-ray study, supported by chemical analysis and density measurements, indicated that the composition is actually $B_{2.89}Si$. The structure is described as similar to boron carbide, except that pairs of silicon atoms take the place of the linear chains of three carbon atoms in B_4C ; the remaining silicon atoms are statistically substituted for some of the boron atoms in the boron icosahedra.

It is interesting to note how recent studies confirm the original work on the silicon-boron system by Moissan and Stock (84). They had reported two intermediate phases, SiB_3 and SiB_6 . SiB_6 has since been described by Adamsky (85) and Cline (86). Zhuravlev (87) had previously reported that SiB_6 is cubic with the CaB_6 structure, but this is apparently incorrect. Adamsky and Cline both obtained single crystals of SiB_6 ; both reported that it is orthorhombic and neither detected the cubic phase mentioned by Zhuravlev. The other silicon boride reported by Moissan and Stock, SiB_3 , is evidently the same as the $SiB_{2.89}$ which Magnusson and Brosset have described.

A detailed x-ray diffraction analysis of the crystal structure of " $B_{13}P_{12}$ " has been completed (82). Analysis of accurately measured single-crystal intensity data showed that in " $B_{13}P_{12}$ " pairs of phosphorus atoms are arranged in "interstitial positions" parallel to the "c" axis, in the positions occupied by the linear chains of carbon atoms in $B_{12}C_3$. The icosahedra in " $B_{13}P_{12}$ ", unlike $B_{2.89}Si$, are made up of boron atoms only; there are no phosphorus substitutions. There is, however, considerable statistical disorder. The sites occupied by the pairs of phosphorus atoms are only 70% occupied; phosphorus atoms also occupy other available interstitial sites statistically. The composition indicated by the x-ray study and density and chemical analyses corresponds to one formula weight of $B_{12}P_{1.8}$ per unit cell (1.e., the ratio of boron to phosphorus is very close to 13 to 2, but the contents of one unit cell include 12 boron and 1.8 phosphorus atoms on the average).

The synthesis of $B_{12}S$, similar in structure to B_6C , has also been described (83). It is very likely that additional representatives of this structure type will be found.

Crystallographic data for alpha boron and for the "boron carbide type" phases are listed in Table IX.

III. Metal-Boron Systems

A. Borides of the Alkali and Alkaline-earth Metals and Aluminum:

Binary borides of the alkali metals have not been reported.

Be-B: Beryllium boride phases corresponding to the approximate compositions Be_2B , BeB_2 and BeB_3 were first reported by Markovskii and co-workers (88). Subsequently Be_2B was found to have the cubic CaF_2 structure with $a = 4.670 \text{ \AA}$ (89). These findings have been verified by Sands and co-workers (19) who prepared and studied single crystals of BeB_2 and BeB_3 , and in addition published a powder pattern of a reaction product labelled " Be_6B' ".

Markovich, Kondrashev and Markovskii (90) have reported the existence of a copper colored beryllium-rich boride, designated as Be_4B or Be_5B . All the lines of this phase are present in the Sands " Be_6B' " pattern (18); the latter also contains, in addition to recognizable impurity lines, a number of lines due to an additional phase, possibly a second beryllium-rich boride.

Becher (91) has mentioned the preparation of BeB_{12} but gave few details. This may be isostructural with the Sands " BeB_6 ", enriched in boron.

Mg-B: The borides of magnesium have not been satisfactorily characterized. Mg_3B_2 , once a favored example of a compound between a divalent metal and boron, does not exist. Russell and co-workers (26) reported that the boride phase in equilibrium with Mg (m) is Mg_3B_2 (AlB_2 type). They found evidence for a tetraboride and two additional higher borides. The latter may correspond to the " MgB_6 " and " MgB_{12} " phases reported by Markovskii and Kondrashev (92). The thermal relations among the magnesium borides

TABLE IX - "Boron Carbide Type" Compounds *

Phase	a (Å)	c (Å)	c/a	$\left[\frac{d(001)}{d(100)} \right]^2$	Ref.
$\alpha-B_{12}$	4.908	12.567	2.561	6.74	74
$B_{12}O_2$	5.37	12.31	2.292	7.00	76
$B_{12}C_3$	5.00	12.12	2.164	6.24	72
$B_{12}P_2$	5.984	11.650	1.980	5.24	75
$B_{12}As_2$	6.142	11.862	1.936	5.00	68
$B_{12}Si_3$	6.370	12.736	2.012	5.40	81
$B_{12}S$	5.50	11.90	2.052	5.61	83

* Reference (71)

have been discussed by Chrétien (93). He found that MgB_2 can be prepared readily at 950°C but that it loses magnesium as the temperature is raised to 1300°C . As more and more magnesium is driven off a tetraboride, and when a hexaboride are formed and finally a phase designated as MgB_x remains, where x varies from 6 to 17. None of the x-ray patterns, aside from that of MgB_2 , has been indexed satisfactorily.

(Ca, Sr, Ba) - B: Calcium, strontium and barium form cubic MeB_6 phases. It has long been believed that these are the only borides formed by these metals, but a tetraboride of calcium with the UB_4 structure has recently been reported (47). Also, Markovskii and Vekshina (36) state that diborides of Ca, Sr, and Ba were prepared by heating the metals with boron in argon at $900 - 1000^\circ\text{C}$. Unfortunately, x-ray diffraction analysis was not used; the products were never obtained pure and their formulas were established on the basis of chemical analysis of the products of hydrolysis in dilute HCl. Additional evidence for the existence of these diborides is needed.

Al-B: This system has been reviewed by Kohn (53). Crystallographic data are listed in Table VIII. The AlB_2 phase is the only aluminum boride whose properties differ significantly from those of boron. Its structure is well known but the others have not yet been determined. With the exception of AlB_2 , the aluminum borides are high melting, very hard and extremely refractory.

Serebrianskii and Epel'baum (94) have reported an investigation of the aluminum-boron system. They prepared the diboride and found that it decomposed slowly to yield only the alpha AlB_{12} phase. They found no signs of either AlB_{10} or of the β or γ polymorphs of AlB_{12} . An investigation of the thermal relations among these phases is needed to resolve these apparent discrepancies.

B. Borides of Rare-earth Metals, Y and Sc:

These have been reviewed by Schneider (5). Up to a few years ago only the hexaborides of a few rare earth metals had been reported. At present the rare-earth borides include compounds of the types MeB_2 , MeB_4 , MeB_6 , MeB_{12} and MeB_{70} (the boron content of the latter has not been precisely determined).

Crystal data for diborides of Y, Sc, Gd, Tb, Dy, Ho and Er are included in Table III. The hexagonal GdB_2 and YB_2 phases listed by Schneider, with lattice constants of 3.83 and 4.45 for the former and 3.78 and 4.40 Å for the latter, are actually metal borates (MeBO_3).

A number of rare-earth MeB_x phases, with x varying from three to four, and with simple tetragonal structures, were described by the present author and co-workers several years ago (42). Subsequent investigations have indicated that these phases cannot be prepared in the absence of carbon and it is likely that the MeB_x phases are borocarbides of unspecified, and possibly variable, boron and carbon content.

Yttrium and all the rare-earth metals, with the exception of europium, form stable tetragonal tetraborides. Yttrium, scandium and the rare-earth metals also form cubic hexaborides of the CeB_6 type. Values of 4.36 and 4.435 Å have been reported for the lattice constant of ScB_6 .

In either case (4.36 or 4.43) the lattice dimension is anomalously large; it is even larger than that of ReB_6 (4.268 Å), which is rather surprising in view of the relative sizes of the two metal¹ in the elementary state ($r_{\text{Sc}} = 1.60$ Å; $r_{\text{Ba}} = 2.16$ Å).

Wide ranges of composition have been noted for EuB_6 (41) and LaB_6 (47) and similar homogeneity ranges may exist in other hexaborides. Powdered hexaborides have characteristic blue to blue-lavender colors; in general, they are good metallic conductors, extremely hard and high melting. Electrical and magnetic properties are discussed in Section IV.

The smaller rare-earth metals (atomic numbers 65 through 71) and γ form cubic dodecaborides (Table VII). These appear to be metallic conductors, but little else is known of their properties. The lattice constants of the rare-earth dodecaborides (Fig. 12) show no anomalies comparable to those of the hexaborides. In its tetraboride, as well as its dodecaboride, the effective valence of the ytterbium atom is +3; it appears to be in the +2 state in the hexaboride.

Borides, very rich in boron (approx. composition MeB_{70}) have been reported for γ (95), Ho, Tb, and Yb (51). These are very hard and very refractory. It is very likely that this phase is also formed by other rare-earth metals.

C. Borides of Actinide Metals:

U-B: Three intermediate phases are known: UB_2 (31), UB_4 (40), and UB_{12} (39). The U- UB_2 eutectic is probably close to 1100°C. (i.e., close to the melting point of uranium: 1132°C), (31). UB_4 appears to be the highest melting uranium boride. A detailed analysis of the crystallography of UB_4 and UB_{12} has been published by Weisheit and Blum (104).

Ti-B: Only two intermediate phases are known: TiB_4 (40) and TiB_6 (49). The crystal structure of TiB_4 was determined by Zalkin and Templeton (40) from single-crystal data. Its melting point is above 2500°C (31) compared with 2200°C for the hexaboride (105). The tetraboride of γ (melting point 2800°C) is also the highest melting of the many boride phases formed by that metal. Little is known of the melting points of the rare-earth tetraborides (other than fragmentary data indicating that CeB_4 melts at a lower temperature than CeB_6 (31)) and the determination of these values would be worthwhile.

Pu-B: Four intermediate phases have been reported (32). The cubic hexaboride has a wide homogeneity range; the lattice constant varies with composition from 4.115 to 4.140 Å. Both PuB_2 and PuB_4 were formed at 1200°C when the boron content of the reaction mix exceeded 70 atomic percent. The tetraboride is isostructural with UB_4 . PuB_2 could be prepared at 800°C but not at 1200°C. In PuB_2 and UB_2 the observed Me-B distances exceed the calculated (Mott²) values by .20 and .34 Å

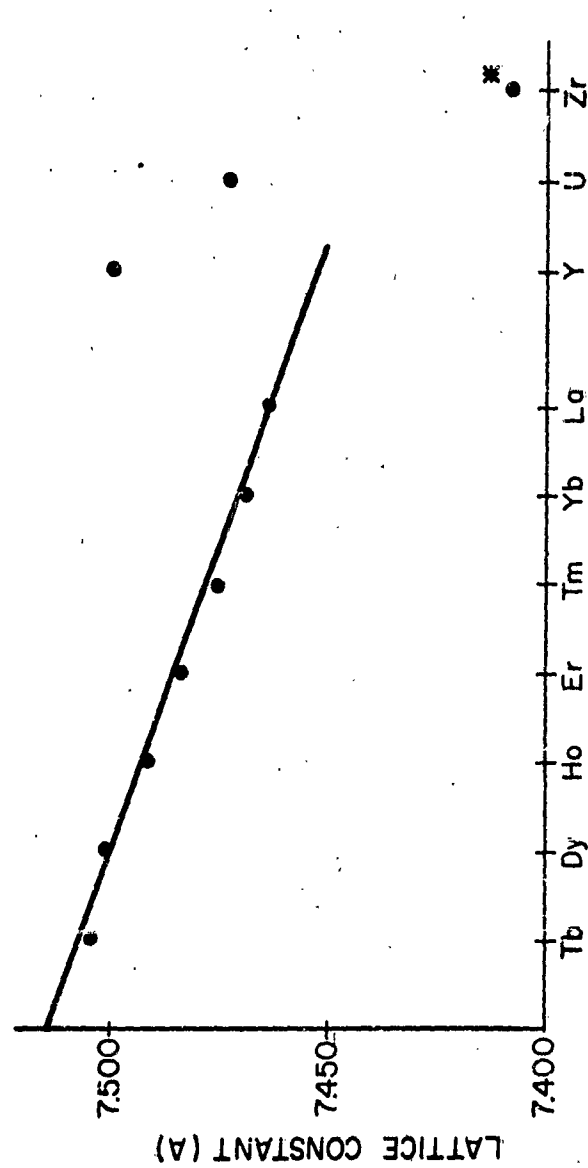


Fig. 12. Unit cell dimensions of MeB_{12} phases.

respectively, whereas in the transition-metal diborides this excess ranges from 0.06--0.08 Å. This may be associated with the anomalously long "c" axis in PuB_2 (3.00 Å) and U_2B_3 (3.99 Å) compared with the transition-metal diborides where the corresponding values range from 2.86 to 3.53 Å.

McDonald and Stuart (32) also report PuB (NaCl structure) with $a = 4.92$ Å. It is felt that the comments made below with respect to Ti, Zr, and Hf are applicable here also and that the presence of oxygen, nitrogen or carbon impurities may have stabilized the "monoboride" phase. It would certainly be worthwhile to re-examine these monoboride phases to establish whether any pure binary NaCl type monoborides exist, or whether all these are actually ternary or quaternary phases.

D. Borides of the Transition Metals of Groups IV, V, VI and VII:

Ti-B: The solid solubility of boron in alpha Ti appears to be very large when its magnitude is estimated from changes of the lattice parameters of titanium-rich alloys (106). However, careful metallographic and analytical studies indicate that the solid solubility of B in alpha Ti is less than .05 weight percent between 750 and 1300°C and close to 0.1 weight percent at the eutectic temperature, 1670°C (97). The discrepancy is probably due to the presence of oxygen or nitrogen in the specimens studied by x-rays.

Titanium forms a stable monoboride (23) and a diboride (2). The former was examined by single-crystal methods and found to be orthorhombic (FeB type) with $a = 6.12$, $b = 3.06$, and $c = 4.56$ Å. It appears that the phase reported, on the basis of powder data, as tetragonal Ti_2B (96) ($a = 6.11$, $c = 4.56$) is actually this orthorhombic monoboride. The orthorhombic unit cell is pseudotetragonal ($a = 2b$) and this could readily lead to the observed misinterpretation of the powder data. The "NaCl-type" TiB phase will be discussed under "Zr-B".

TiB_2 is extremely stable, an excellent thermal and electrical conductor, and it melts at 2900°C (30). The constitution diagram from 0-70 atomic percent boron has been published (97).

Zr, Hf-B: Cubic TiB , ZrB , HfB and PuB phases with the NaCl structure have been reported frequently (96, 7, 8, 32). The evidence concerning these is often confusing but it appears that in most, or all of these, variable amounts of carbon, nitrogen or oxygen were present to stabilize the NaCl structure. It is probable that true binary NaCl type monoborides of Ti, Zr and Hf do not exist; a careful re-examination of the PuB preparation with rigorous exclusion of possible contaminants would be in order.

Zr, and Hf, like Ti, form very stable, hard and high-melting diborides. Their homogeneity ranges appear to be narrow (30). ZrB_2 melts at 3050, HfB_2 at 3250°C (30). All three are excellent electrical conductors with reported resistivities of about 10 $\mu\text{ohm-cm}$ (4). These measurements were made on powdered specimens and the electrical resistivities of single crystals may be substantially smaller.

$\text{ZrB}_{1/2}$ is stable above 1600°C and melts at 2680°C (55, 98). Efforts to prepare the analogous dodecaboride of Hf were unsuccessful. A tentative phase diagram of the Zr-B system has been published (98).

V-B: Four intermediate phases are known: V_3B (22), VB (24), V_3B_4 (99) and VB_2 (2). There do not appear to be any stable higher borides of vanadium. The existence of at least one additional phase, possibly a high-temperature polymorph of V_3B_2 , is indicated by observations of Hardy and Hulm (107) on arc melted V-B specimens. Nb, Ta-B: Tentative phase diagrams for the Ta-B, Nb-B and V-B systems have been published by Kieffer and Benesovsky (108).

Borides of the following types: Me_3B_2 (22), MeB (1e,c), Me_3B_4 (1e,c) and MeB_2 are known. NbB , Nb_3B_4 (1e) and TaB and Ta_3B_4 (1c) have narrow homogeneity ranges; the wide homogeneity ranges observed in TaB and NbB_2 (1e, c, 31) (and possibly in VB_2) have been discussed in Section II (diborides).

Kiesling noted that Ta_2B (1c) could never be obtained in pure form; it was always accompanied by either Ta (m) or TaB; the analogous Nb_2B phase has not been reported.

Recent work by Leitnaker (110) helps to clarify this point. It was found that all the tantalum borides lose boron by evaporation at high temperatures. Below 2040°C Ta_2B disproportionates to yield Ta_3B_2 plus $Ta(m)$. Above 2180°C Ta_3B_2 in turn disproportionates to form Ta_2B and TaB . These reactions are indicated schematically in Fig. 13.

Leitnaker (110) has also noted that the composition of the " Ta_2B " phase is actually close to $Ta_{2.4}B$ and " Ta_3B_2 " is actually $Ta_{3.2}B$. The reaction with boron was found to yield TaB_2 ; TaB plus $Ta(m)$ yielded TaB . No signs of " Ta_3B_4 " were detected.

Cr_2B : " Cr_4B " has been described by Bertaut and Blum (12), but Kiessling (1b) and Epel'baum (100) do not list Cr_4B as an intermediate phase in the chromium-boron systems. Cr_2B (12), Cr_3B_4 (1b) and CrB_2 (1b) have been reported by many authors. There can be little doubt about the existence of Cr_2B , Cr_3B_4 , and Cr_3B_5 , but there are differences of opinion about the conditions under which these phases may be prepared (7t). Epel'baum (100) has also reported a boron-rich compound, CrB_6 , which had not been detected by earlier workers.

Elfstroom (25) has subjected the crystal structure of Cr_3B_4 to a careful re-examination and found that the double boron chains previously described (1b) did exist, but that no anomalously short boron-boron bonds were present. Kiessling (1b) had reported such short bonds between boron atoms in adjacent chains.

The chromium borides are metallic, very hard and generally resistant to chemical attack. They dissolve in perchloric or hot sulfuric acid.

Mo_2B : Kiessling (1a) first reported on the Mo_2B , MoB and Mo_2B_5 phases. In the course of examination of the Mo-B system (20), the Mo_3B_2 phase and two others, stable above 1600°C were discovered: β - MoB and MoB_2 . It was observed that neither " Mo_2B_5 " nor " MoB_2 " have the ideal compositions indicated by their formulas; both had variable boron content, somewhat higher than that corresponding to the MoB_2 formula and lower than the Mo_2B_5 value.

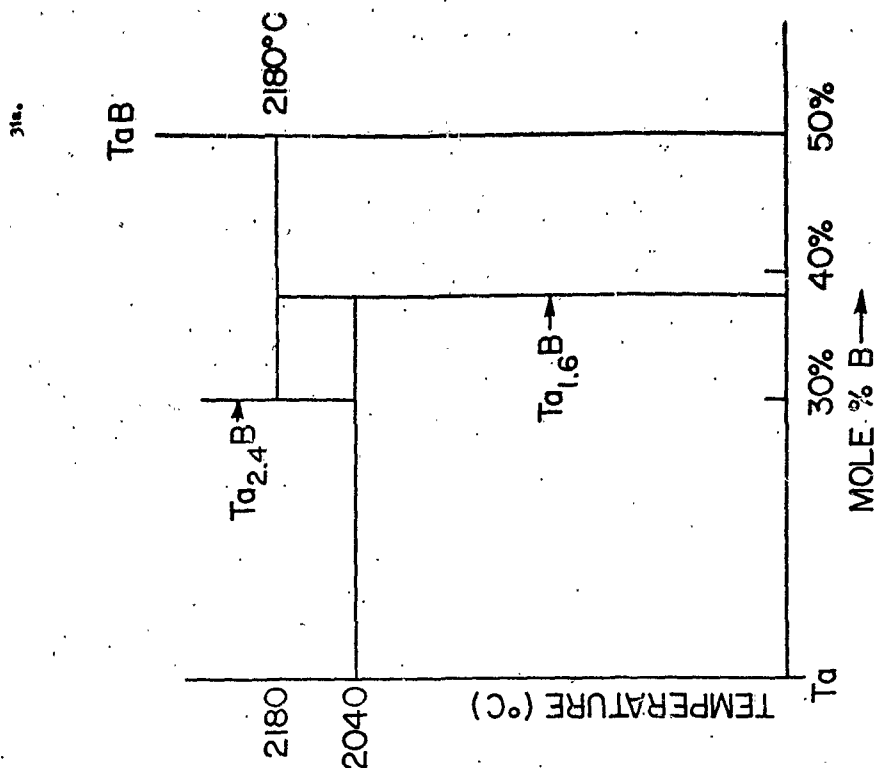


Fig. 13. Phase relationships in the Ta-B system.

W_2B_5 : Similar phases, but with some significant differences, exist in the W-B system. W_2B , WB , and W_2B_5 (1a) are well established; a high temperature modification of WB , analogous to that found in MoB , has been reported (96) but no W_2B_5 phase has been detected. W_2B_5 differs from Mo_2B_5 in that it is hexagonal while the latter is rhombohedral. The atomic arrangements are very similar in both phases.

Chrétien and Helforaky (46) have reported the preparation of MoB_4 and WB_4 ; the two phases are isomorphous and their tetragonal unit cells have almost identical dimensions. Thermal stability studies showed that pure MoB_4 and WB_4 dissociate at 1600° to yield Mo_2B_5 and MoB (or W_2B_5 and WB). When small amounts of carbon were present the dissociation of WB occurred at $1400^\circ C$. Phase relations in the W-B system have also been discussed by Samsonov (101) who, however, did not detect WB_4 .

Chrétien's study indicates that the following two phase regions exist in the W-B system:

I	II	III	IV	V
W	W_2B	WB	W_2B_5	WB_4
plus	plus	plus	plus	plus
W_2B_5	WB	W_2B_5	WB_4	B

Small amounts of unreacted tungsten were detected in region II; some unreacted boron was detected in each region except for III.

Brewer (31) found that W_2B_5 decomposes within nine minutes at $1810^\circ C$; tetragonal WB decomposed in fifteen minutes at $2040^\circ C$ but W_2B was stable at the latter temperature. The reaction of W_2B with graphite yielded WB , WC and unreacted C.

The Mo-B system was very similar to the W-B system.

$Mn-B$: Kiessling (1d) investigated the MnB system and determined the crystal structures of Mn_4B_3 , Mn_2B , MnB and Mn_3B_4 . The extensive homogeneity range of Mn_4B_3 has been discussed above.

Kiessling did not observe borides richer in boron than Mn_3B_4 . Recently, MnB_2 (AlB_2 type) was prepared (96) but it is evidently far less stable than most transition-metal diborides. Fruchart (37) has reported that MnB_2 decomposes to Mn_3B_4 and MnB_4 on slow cooling. The powder pattern of the latter has not been indexed, but it is unlike that of other tetraborides.

$Re-B$: The tetragonal Re-B phase with $a = 5.47$ and $c = 4.73$ Å which had been reported by Mashpor et al (102) has not been detected by subsequent investigators. Aronsson (103) and co-workers have described the crystal structures of Re_3B (15,16) and Re_9B_3 (15). The phase richest in boron appears to be ReB_2 , whose crystal structure bears marked resemblances to those of W_2B_5 and Mo_2B_5 (36).

5. Borides of Metals of Group VIII:

$Fe-B$: Boron is only slightly soluble in alpha, beta or gamma iron; details of the phase diagram, at very low boron concentrations (0.001 to 0.025 wt. percent) are given by Hansen (3).

Fe_2B is tetragonal ($CuAl_2$ type). FeB appears to exist in two polymorphic modifications. Fruchart (111) found that the diffusion of boron into iron at $750^\circ C$ to form the monoboride yields a new modification of FeB ; this transforms to the "normal" orthorhombic form (Table II) when it is heated above $1200^\circ C$. The direct reaction of iron with an equal part of boron at $1200^\circ C$ also yields the orthorhombic modification (labelled beta FeB by Fruchart).

$Co-B$: Co_2B (2) and CoB (2) exist in narrow homogeneity ranges. Rundqvist (13) has reported a cobalt-rich boride, Co_3B , with the cementite structure and this has been confirmed by Fruchart (111).

$Ni-B$: The nickel-boron system has been studied in detail by Rundqvist (21) in the range of Ni_3B to NiB . Single-crystal and powder methods were used. Intermediate phases are: Ni_3B (cementite type), Ni_2B ($CuAl_2$ type), Ni_4B_3 (orthorhombic), Ni_4B_3 (monoclinic) and NiB (CrB type). Ni_3B , Ni_2B and NiB had been reported by

others, but the two Ni_4B_3 phases had not been detected previously. The following two-phase regions were found: Ni_3B plus Ni_2B , Ni_2B plus orthorhombic Ni_4B_3 , orthorhombic Ni_4B_3 plus monoclinic Ni_4B_3 , monoclinic Ni_4B_3 plus Ni_3B . The orthorhombic Ni_4B_3 had a wide range of homogeneity; no such range was detected in the monoclinic form. The temperature ranges of stability of these two forms of Ni_4B_3 were not established. No borides richer in boron than Ni_4B were found.

Rundqvist (21) has noted that this series of five nickel borides provides a striking example of the increasing tendency for boron-boron bond formation with increasing boron content, to which Klessling had first drawn attention (1f).

F. Platinum Metals-Boron:

The borides of the platinum metals have been the subject of a series of investigations by Aronsson and co-workers at the University of Uppsala (11,15,17).

Using powder and single-crystal x-ray techniques, they have determined the crystal structures of Ru_7B_3 , Rh_7B_3 (and Re_7B_3), and demonstrated that these are of the Th_7Fe_3 type (15). PtB and $\text{RhB}_{1.1}$ were shown to have the hexagonal, anti-NiAs structure, and $\text{IrB}_{1.1}$ was found, surprisingly, to crystallize with the ThSi_2 structure.

Aselius has carried out a precise determination of the crystal structure of Ru_{11}B_8 (8c) in which both single and double boron chains were found. Stenberg (14) has studied Pd_3B and Pt_3B_2 ; the former has the orthorhombic cerentite (Fe_3C) structure; the latter is monoclinic and isomorphous with Mn_2C_2 .

Aronsson has shown (15) that the "orthorhombic Rh_2B " described by earlier workers (18), was very probably Rh_2Si . He also confirmed earlier observations (112) to the effect that the powder photographs of $\text{RuB}_{1.0}$ and $\text{OsB}_{1.0}$ could be indexed on the basis of cubic unit cells (15).

Recent work by Kempter and Fries (33) is of interest in this connection.

They studied the Os-B and Ru-B systems and reported the preparation of OsB_2 and RuB_2 phases with the hexagonal AlB_2 structure, and Os_2B_5 and Ru_2B_5 with the W_2B_5 structure.

It will be noted (Table III) that $a = c$ in both OsB_2 and RuB_2 and their powder patterns could, therefore, be indexed on the basis of relatively large cubic unit cells (112) but there can be little doubt that the hexagonal indexing is correct and that cubic RuB and OsB do not exist.

G. Borides of Gold and Silver:

Although the literature contains many statements to the effect that neither gold nor silver react with boron to form intermediate phases (3), Obrowski (34) remained skeptical and has prepared the hexagonal diborides of both metals by direct reaction. There is a moral in this somewhere.

IV. Properties of Borides

Our knowledge of the properties of the refractory binary borides is scattered and fragmentary. The diborides and hexaborides have been investigated most intensively, but even for these phases the available data are generally inadequate and sometimes unreliable. Pure boride phases are difficult to prepare and their stoichiometry is often uncertain. As a result, inadequately characterized specimens have often been used for the determination of properties. Some efforts have been made to exclude data of doubtful validity from this Section. These cannot be wholly successful and the reader is urged to view the results reported here, particularly those dealing with impurity sensitive properties, as essentially tentative.

A. Stoichiometry:

Gross deviations of indicated compositions of borides from their accepted chemical formulas have been reported with disturbing frequency, usually when precise control has been maintained over the specimen composition, or when the latter has been subjected to careful chemical analysis.

Recently, Kempter and Fries (33) reported the preparation of RuB_2 and OsB_2 (AlB_2 type) and Ru_2B_5 and Os_2B_5 (M_2B_5 type). The osmium "diboride" phase was obtained when equal atomic proportions of boron and osmium were heated at either 1300 or 1685°C. When two parts of boron were heated with one of osmium at 1300°C, the product consisted mainly of " Os_2B_5 " plus a minor amount of the "diboride". Similarly, when five atomic parts of boron were heated with two of ruthenium, the product consisted mainly of an unidentified phase*, plus only minor amounts of the expected Ru_2B_5 phase.

*Roof and Kempter (144) have recently reinvestigated the Os-B and the Ru-B systems in order to characterize the "unidentified phase" referred to above. Using single-crystal and powder x-ray methods they have shown that both Os and Ru form orthorhombic diborides of a previously unreported type. The space group is $Pmmn$ and the cell dimensions are:

RuB_2	$\frac{a}{4.644}$	$\frac{b}{2.867}$	$\frac{c(A)}{4.045}$	$\frac{\text{density (calc.)}}{7.567}$
OsB_2	4.683	2.872	4.076	12.83

Similar deviations from the accepted chemical formulas have also been reported by Brewer and co-workers (31); they found that the composition of " TaB_2 " varied, without change of structure, from $TaB_{1.78}$ to $TaB_{2.37}$, and similar results are indicated for NbB_2 .

A study of palladium borides revealed that the chemical composition of the phase conventionally labelled Pd_3B_2 is actually $Pd_{3.28}B_2$ and that the composition of " Pd_3B " is $Pd_{2.85}B$ (14). Aronsson (15) has described a boride phase with the composition $IrB_{1.1}$. This has the $ThSi_2$ structure and, in terms of that structure, almost 50 percent of the boron atoms are absent.

Kiessling (1a) and Steinitz (20) have found that the " Mo_2B_5 " phase is deficient in boron; chemical analyses consistently indicated that the boron content ranged from 19.5 to 20.8 weight percent instead of the expected 22 percent.

A wide range of homogeneity has also been detected in LaB_6 (47). The boron content varies from 85.8 to 88 atomic percent, corresponding to compositions from LaB_6 to $LaB_{7.35}$. The Mn_4B phase described by Kiessling (1d) is another example of a striking deviation from the ideal composition. This phase was described in terms of the Mn_2B structure, from which half of the boron atoms are absent. There are indications that a continuous range of compositions from Mn_4B to Mn_2B could be prepared with the " Mn_2B " structure.

In the Be-B system (19) the x-ray pattern of the BeB_6 is almost identical, with respect to intensities and "d" spacings, with that of one of the tetragonal polymorphs of boron (54). The suggestion has been made (19) that this Be-B phase may have a range of homogeneity extending all the way from BeB_6 to pure (tetragonal) boron.

Similar results have been reported for boron carbide (138). This phase was found to be stable over a very wide range of composition, and it was concluded that very little significance could be attached to the " $B_{4.0}$ " formula usually assigned to it. The recent description of the alpha form of rhombohedral boron (74),

which is isostructural with boron carbide; lends added weight to the notion of an extended range of carbon content in the latter, possibly from pure boron to B_4C .

A detailed single-crystal structure analysis of " $B_{12}P_{12}$ " has recently been completed (82). This substance, like boron carbide, is isostructural with alpha boron. The composition of the crystal studied was found to be close to $B_{12}P_{11.8}$ (i.e., there are twelve boron atoms and 1.8 phosphorus atoms in each unit cell). The phosphorus sites in the structure are only partially and apparently randomly occupied. It is very likely that similar ranges of composition will be found in other representatives of the boron-carbide structure type (See Table IX).

Leitnaker and co-workers (109) have reported that " Ta_2B " has an actual composition corresponding to $Ta_{2.4}B$ and that the composition of the phase generally referred to as Ta_3B_2 is closer to $Ta_{3.2}B_2$.

As a more careful work is reported this list will expand. There is, fortunately, evidence that at least some of the binary borides possess narrow ranges of homogeneity. The diborides of Group IV transition metals fall into this category (70). Eick and Gilles found no detectable variation of lattice parameters of rare-earth tetraborides with composition and the same appears to be true of the rare-earth metal dodecaborides (57) and many of the lower borides (11). Nevertheless, it is evident that the physical significance to be attached to chemical formulas of many of the borides should be subjected to careful reappraisal. Where the stoichiometry is either not established, or is open to question, it is probably best to describe phases mainly in terms of structure types without attaching undue importance to specific chemical compositions.

B. Chemical Reactivity:

Schwarzkopf has discussed the chemical properties of borides of Groups IV, V, and VI metals (4). All are said to be readily decomposed by fusion in molten alkali hydroxides or carbonates. All oxidize in air at elevated

temperatures, and show varying degrees of resistance to attack by mineral acids; TaB_2 and NbB_2 are reported to be most resistant to such chemical attack. They are unaffected by HCl and HNO_3 and are attacked only slowly by hot sulfuric and hydrofluoric acids.

Markovskii and Kaputovskaya (115) have also studied the chemical behavior of a number of transition-metal diborides. With the exception of the Cr, Nb and Ta compounds, all were reported to dissolve in cold nitric acid. CrB_2 dissolves in hot nitric acid. NbB_2 and TaB_2 dissolve only in HF. ZrB_2 was said to be relatively poor in its resistance to HCl, but TiB_2 is not attacked by this reagent.

These findings agree only in part with those reported by Kodylevskaya and Samsonov (113), who studied the resistance of borides of Ti, Zr, Nb, Ta, Cr, Mo and W to ~~hydrofluoric~~ the common acid and alkaline solutions. The diboride of chromium was reported to be most soluble, and TaB_2 and NbB_2 the least soluble, in pure acids. TaB_2 resists acid mixtures best. MoB_2 is poorest in this respect. Fusion with NaOH dissolved all the specimens.

Kiessling (1b), on the other hand, reported that the chromium borides are resistant to solution in all the common acids except perchloric. Kiessling and Liu (131) have studied the thermal stability of chromium, iron and tungsten borides in the presence of ammonia at 1180°C. In all cases the borides

reacted to form boron nitride and a metal nitride. The stability of chromium and iron borides in the presence of the ammonia was found to increase with increasing boron content, indicating to the authors that strong boron bonds are present in the higher borides. The findings also indicated that the strength of the metal to boron bond decreases with increasing atomic number of the transition metal (See also Table IV).

Brewer and Hareldsen (127) found that ZrB_2 , NbB_2 and W_2B are stable to nitrogen at 1550°C. TiB_2 was found to react with nitrogen at that temperature to form TiN , but was stable at 2000°C. The high-temperature reactions of carbon and nitrogen

with transition-metal borides indicated that the stabilities of those studied were the borides of Ti, Zr, Nb and Ta.

The lower borides of beryllium (e.g., Be_2B) are reported to be very poor in their resistance to attack by oxygen, nitrogen and carbon at elevated temperatures (114). Higher borides, such as BeB_2 and BeB_3 were generally stable up to 800-900°C. These results are consistent with the findings of another group that the stability of beryllium borides in mineral acids increases with increasing boron content of the compound (88).

Magnesium and aluminum diborides are readily soluble in dilute acids, but the higher borides of both metals are substantially more resistant to chemical attack (26, 53).

Vekshina and Markovskii (142) have studied the chemical properties of the alkaline-earth hexaborides and find that they are approximately as resistant to chemical attack as the transition metal diborides. They withstand attack by acids and alkalis (except for nitric acid); they are stable in nitrogen gas at high temperatures and do not react with carbon at temperatures up to 2000°C. At temperatures above 600°C they oxidize rapidly in air, although even this process is apparently slowed by the formation of an adherent oxide film on the borides.

Brewer and Haraldsen (127) found that the hexaborides of Ce and Th, and the diborides of Ti, Zr, Nb and Ta, as well as all borides of Cr, are stable in the presence of carbon up to the highest temperatures attained in their experiments.

C. Thermal and Mechanical Properties:

Coefficients of thermal expansion of diborides and hexaborides are listed in Tables X and VI. The coefficients are generally very small, much smaller, in most instances, than those of the pure metals. In only one case (the expansion of VB_2 in the "c" direction) does the coefficient exceed 10×10^{-6} per degree. The reported anisotropy of thermal expansion of this phase (i.e., VB_2) is extraordinarily large (15.9 to 3.8); the measurements are very likely in error.

Published values of the heats of formation of various borides are listed in Table X.

Leitnaker and co-workers (110) have calculated molar heats of formation of several compounds, starting from the assumption that ΔH_f of ZrB_2 is close to -71.7 kcal. per mole. On this basis it was established that ΔH_f of Ta_2B_3 , Ta_4B_6 , and TaB_3 all lie within the range -38.4 to -64.9 kcal., and that limits of -22.7 to -51.7 could be set for TaB_2 and -20.0 to -26.0 for W_2B .

There is considerable uncertainty regarding the correct value of ΔH_f of TiB_2 . Brewer and Haraldsen (127) had reported -71.4 kcal., and Samsonov has recorded a value of -70.04 kcal. (8a). Williams (128) has repeated and refined some of his earlier work on TiB_2 and has reported that $\Delta H_f = -50 \pm 5$ kcal. per mole.

The elastic constants of TiB_2 have been measured by Gilman and Roberts (135). These are:

C_{11}	10^{12}	dynes/cm. ²	6.9
C_{33}			4.4
C_{44}			2.5
C_{12}			4.1
C_{13}			3.2

The Debye characteristic temperature of $1003 \pm 10^\circ \text{K}$ has been computed from these values of the elastic constants (135). This may be compared with a Debye temperature of $990 \pm 30^\circ \text{K}$ computed from single-crystal x-ray diffraction data (141). The very high value of the Debye temperature is consistent with other known properties of the material, e.g., its very high melting point and its great hardness.

The x-ray data for TiB_2 have also been analyzed to yield values of the root-mean-square amplitudes of thermal motion of the boron and titanium atoms. At 300°K these are:

	Parallel to "c" (in Å)	Perpendicular to "c" (in Å)
B	$.063 \pm .003$	$.067 \pm .003$
Ti	$.046 \pm .001$	$.052 \pm .001$

The similarities between the amplitudes of motion parallel to and perpendicular to "c", and between the coefficients of thermal expansion in the different directions, reflect the pseudo-isotropic character to TiB_2 (141).

TABLE X: Properties of Transition-Metal Diborides

Compound	Microhardness kg/mm ²	Ref.	Coefficients of Linear Thermal Expansion ($\times 10^6$)		ΔH_f K cal/mole	Ref.
			α_a	α_c		
TiB ₂	3400	133	5.6	6.6	-71	127**
VB ₂	2070	76	3.8	15.9	-24	8a
CrB ₂	1800	76	6.0	6.7	-31	127
ZrB ₂	2200	4	5.6	5.5	-27	127
HfB ₂	2200	76	5.9	8.4	-36	127
MoB ₂	1200	20	7.6	7.8	---	---
Co ₂ B ₅	2330	20	---	---	---	---
FeB ₂	2900	116	5.3	5.3*	-74.2	116
TaB ₂	2500	76	5.2	5.9	-51.7	110
W ₂ B ₅	2600	101	---	---	---	---

* (116) reports $\alpha = 5.73 \times 10^{-6}/\text{deg.}$ (dilatometric)** (128) has reported ΔH_f of TiB₂ = -50 ± 5 Kcal/mole**D. Magnetic Properties:**

The magnetic properties of manganese-boron alloys have been studied by Kharasov and Parsanov (119). Twenty alloys, ranging in composition from 5 to 52 weight percent of boron, were prepared. Four Mn-B phases were detected, of which only MnB was ferromagnetic. The spontaneous magnetization rose sharply at 37 percent boron and reached a maximum at 50 percent boron. The MnB phase could be detected when more than 33 percent of boron was present. The spontaneous magnetization of MnB at room temperature is 140 ± 1 gauss. cc/gm, suggesting its possible use as a magnetic material. The ferromagnetic Curie temperature of MnB is $289 \pm 40^\circ\text{C}$. The magnetic susceptibility of low-boron alloys reached a maximum at $220-240^\circ\text{C}$; a second maximum was observed at $285-295^\circ\text{C}$ when more than 32 percent boron was present.

Fruchart (111) has studied the iron-boron system. He found that both Fe₂B and FeB are ferromagnetic with Curie temperatures of 742 and 309°C respectively.

Lundqvist, Meyers and Vestin (132) have measured the paramagnetic susceptibilities of a number of monoborides over a wide range of temperatures. VB, CrB and MB are paramagnetic and were investigated in the temperature range 150°K to 800°K ; MnB, FeB and CoB are ferromagnetic and were studied from their respective Curie points to 800°K .

VB and CrB are strongly paramagnetic. Their susceptibilities decrease markedly between 100 and 500°K and show little variation above the latter temperature. The susceptibilities are accurately described by Weiss-Curie relations as follows:

$$\chi_{VB} = \frac{2.9 \times 10^{-3}}{T + 220} \text{ emu} \quad \text{(for } T < 350^\circ\text{K)}$$

$$\chi_{CrB} = \frac{2.6 \times 10^{-3}}{T + 930} \text{ emu}$$

MB manifests very weak, temperature independent, paramagnetism

($\chi = 4.0 \times 10^{-5}$ e.m.u.). This is interpreted in terms of a filled d band; the slightly positive susceptibility is attributed to conduction-band paramagnetism.

The ferromagnetic Curie temperatures reported by Lundqvist, et al. for MnB and FeB (578 and 598°K) are in fair agreement with values reported previously (562°K (119) and 581°K (117)).

Juretschke and Steinitz (136) have measured the magnetic susceptibilities of a number of transition-metal diborides; all are weakly paramagnetic except for ZrB_2 which is diamagnetic.

Magnetic properties of various hexaborides are listed in Table XI. These are particularly useful as guides to the effective valence states of the metal atoms in those compounds. The data indicate that all the metals listed, with the possible exception of Sm, are in the Me^{+3} state in the hexaborides. For example, the calculated moment for Ce^{+4} is zero, and in view of the fair agreement between the observed moments (2.91 and 2.30) and that calculated for Ce^{+3} , we may exclude the tetravalent configuration from consideration. In the case of Sm, the experimental moment in the hexaboride is approximately halfway between the values calculated for Sm^{+3} (1.60) and Sm^{+4} (3.45).

The indicated Yb^{+3} configuration in the hexaboride is puzzling. The anomalously large size of the YbB_6 unit cell has been attributed to the effective divalent character of Yb in the hexaboride. This hypothesis appears to be ruled out in view of the close agreement between experimental values of the magnetic moments and those calculated on the assumption that the Yb ion is in the $+3$ state (i.e., 4.58 vs 4.50 for Yb^{+3}). However, the analysis of Hall effect and resistivity measurements indicates that there are only 0.05 conduction electrons per metal atom in YbB_6 (Table XIV). The latter may be reconciled with the notion of divalent Yb in YbB_6 if the assumption is made that each metal atom contributes two electrons to the boron lattice to stabilize the latter (See "Bonding" below). Measurements of the effective magnetic moments of the Lu atom in LuB_6 may help to resolve this apparent contradiction.

Coles and co-workers (117a, b) have reported antiferromagnetic behavior in GdB_6 at low temperatures; a distinct maximum in the magnetic susceptibility plotted against the absolute temperature occurs at 44°K. Direct interactions among the metal-ion cores are considered unlikely in view of the large $Me-Me$ distances (4.10 Å). The observed effect was attributed to indirect antiferromagnetic

TABLE XI - Magnetic Properties of Hexaborides

Compound	μ_{exp} Ref: (120) (117) (89)	μ_{calc} (μ_B) $+3$	θ_p (°K) Ref: (120) (117)
YB_6	0	0	---
LaB_6	0	0	---
CeB_6	2.91	2.30*	-344
PrB_6	---	3.37	---
YbB_6	3.82	3.43*	-455
SmB_6	---	2.52**	---
GdB_6	7.63	7.78	-49
LuB_6	4.36	---	-2

* Exhibited Weiss - Curie behavior from about 350 - 750°K; susceptibilities were measured in those temperature ranges and extrapolated to 25°K.

** Exhibited non-Weiss-Curie behavior; the susceptibility rose with increasing temperature.

μ = magnetic moment in Bohr magnetons

θ_p = paramagnetic Curie temperature.

interactions among the 4f ions which are assumed to take place via the one conduction electron which is present for each Gd atom (117b).

Only one investigation of the magnetic properties of a higher boride has been reported. Bartaut and Blum (49) established that UB_{12} is diamagnetic.

E. Electrical Properties:

This Section will be concerned mainly with the electrical properties of various transition-metal diborides and rare-earth and alkaline-earth hexaborides, i.e. with the only groups that have been studied systematically. Only scattered bits of information are available concerning other borides; these will be dealt with first.

Johnson and Deane (47) noted that LaB_4 is metallic in appearance, and is presumably an electronic conductor, but gave no numerical details. Fruchart (111) reported that Ni_3B is metallic, with a resistivity of 25.5 microhm-cm. The resistivity of 65-percent dense VB is 65 microhm-cm.; extrapolation to 100 percent density indicates that the fully dense material should have a resistivity of about 35-40 microhm-cm. (24). Resistivities of 64 microhm-cm. have been reported for both NiB and CrB (4).

NbB becomes superconducting at 8°K (145); of the large number of borides whose possible superconductivity has been investigated, only Ta_2B , W_2B and Nb_2B show superconductivity at temperatures greater than 1.28°K (107).

The thermoelectric coefficients of various monoborides have been measured by Lundqvist et al at several temperatures (132). Their results are listed in Table XII. The indicated thermoelectric powers of these materials are low and none shows great promise for thermoelectric applications, but the data are useful for studies of electron properties. These results, in conjunction with the magnetic data for these phases, to which reference has been made above, have been interpreted as indicating that the properties of a boride of composition M_zB , where z is the atomic number of the metal, may be correlated with those of the pure metal of atomic number $z + 1$ (132).

TABLE XII - Thermoelectric Powers of Monoborides

Compound	(vs. silver) (in microvolts per degree)*			
	0°C	50°C	100°C	150°C
CrB	-0.6	-0.6	-0.5	-0.5
NiB	+6.8	+6.8	+6.6	+6.5
FeB	-6.8	-6.4	-3.9	-0.7
NbB	+3.0	+3.5	+4.0	+4.7

* Reference (132)

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Hall constants, resistivities and thermoelectric coefficients of various transition-metal diborides are listed in Table XIII. The data reported by I'vov, Nemchenko and Samsonov (125) are the most recent; agreement with comparable values reported some years previously by Juretschke and Steinitz (136) is surprisingly good. In general, measurements of impurity sensitive properties, such as electrical resistivity, show a wide scatter; in column 7b we have listed resistivity values assembled by Aronsson (7b) which are considered to represent the limits within which the correct values may be expected to fall. Variation of porosity of the sintered polycrystalline specimens used for these measurements and the probable presence of impurities in many of them are the chief causes of the wide ranges reported. The resistivities determined by Juretschke and Steinitz were corrected for porosity effects.

Data in the column headed "(146)" in Table XIII were published more than thirty years ago by Moers. Although the compounds were identified only as "borides", the magnitudes of the resistivities and the similarities between the melting points listed by Moers and those given in Table IV, leave little room for doubt that the phases referred to were actually diborides. Impurities, in the form of the pure metals, oxides, free boron or other boride phases, could only have raised the indicated resistivities and lowered the melting points.

The usefulness of single-crystal measurements should be pointed out again here. These would represent measurements on relatively pure, single phases, would yield information on the anisotropy of the resistivities, would make possible more reliable magnetic and thermoelectric measurements, and would eliminate grain boundary effects.

In comparing the results reported in (125) with those of (136) (Table XIII), the remarkably good agreement among the Hall constants in the two sets of data should be noted. All the transition-metal diborides have negative Hall constants (with the possible exception of Mo_2B_3); both sets of measurements indicate very large negative magnitudes of R for diborides of Group-IV metals and much smaller magnitudes for the others.

TABLE XIII: Electrical Properties of Transition Metal Diborides

Compound	Ref: 125			Ref: 136			Ref: 7b			Ref: 146		
	R	ρ	α	R	ρ	α	vs Cu	ρ	α	ρ 20°C	ρ -180°C	ρ -180°C
TiB ₂	-17.8	14	-5.1	-24	9	---	9.7	9-15	---	15.2	3.7	---
ZrB ₂	-17.6	17	+1.2	-20	7	---	5.8	7-10	---	9.2	1.8	---
HfB ₂	-17.0	12	---	-17	15.8	---	---	10-12	---	10	---	---
VB ₂	-1.1	16	---	-1.1	38	---	2.5	16-38	---	16	---	---
NbB ₂	-2.1	34	-1.4	-1.0	12	---	4.3	12-65	---	---	---	---
TaB ₂	-2.2	37	-3.1	-2.7	14	---	5.0	14-68	---	---	---	---
CrB ₂	-1.1	21	-6.8	-1.1	56	---	10.0	21-56	---	---	---	---
Mo ₂ B ₅	+0.1	25	+3.2	-0.5, +0.5	30	---	0	18-45	---	---	---	---
W ₂ B ₅	-1.7	43	+3.2	-1.6	39	---	0	21-56	---	---	---	---

R = Hall coefficient in cc. per coulomb ($\times 10^4$)

ρ = Resistivity in microhm cm.

α = Thermoelectric coefficient in microvolts per degree.

Juretschke and Steinitz interpreted their data on the basis of a model whose electrical conductivity is mainly due to electrons in one energy band. The large negative Hall constant of the Group-IV metal diborides then implies that in these compounds there is a small fractional number of conduction electrons in this band. The band is nearly empty; it is either separated by an energy gap from the next lower one or overlaps another band slightly. In the diborides of Group-V and VI metals the band then fills to the extent of about one additional conduction electron per unit cell. (Juretschke and Steinitz made detailed measurements of a large number of solid solutions between TiB_2 and VB_2 , and between VP_2 and CrB_2 , in addition to the pure phases listed in Table XIII.) The Hall constants in the diborides of the Group-V metals are negative but their values are closer to "normal"; there is about one electron per unit cell in the conduction band in these compounds. The mobilities of conduction electrons in the Group-IV compounds are in the range 200-300 $cm^2/v\cdot sec$; these values decrease by factors of about fifty in the Group-V and VI compounds.

It is suggested (136) that the band structures in these diborides are very similar to those of the parent metals, and that the three valence electrons of each boron atom participate in the occupation of the metal d bands. This leads to a lowering of the centers of gravity of these bands, both in an absolute sense and relative to the next higher s band. In TiB_2 the 3d band would be effectively filled by the six boron electrons and would overlap with $4s$, giving a small number in that band. This model accounts in a remarkably simple way for many aspects of the Hall data, for the electrical resistivity of the pure TiB_2 , VB_2 and CrB_2 phases and the solid solutions among them, and for the weak paramagnetism observed in these compounds. Some less satisfying aspects of the Juretschke-Steinitz model will be discussed in the next Section, under "Bonding".

The thermoelectric coefficients and the temperature dependence of the coefficients of transition-metal diborides and their solid solutions have also been

measured (149). Results are shown in Figs. 14, 15. These indicate a systematic change of thermoelectric power with composition of the solid solution, but cannot be explained on the basis of the simple one-band model postulated by Juretschke and Steinitz (136) to explain their measurements of Hall constants and electrical resistivities. (It should be noted that the specimens used for these thermoelectric measurements were the same ones used previously by Juretschke and Steinitz.)

The electrical properties of the rare-earth and alkaline-earth borides have been investigated in detail by Paderno and Samsonov; in two comprehensive papers (124, 139) these authors have listed not only their own findings but also large amounts of data from other sources. Selected portions are presented in Table XIV.

From room temperature to about 800°C, and possibly higher, these phases all behave like metallic conductors. The relatively high resistivity of the alkaline-earth hexaborides, particularly CaB_6 , is in agreement with a qualitative observation made by Lafferty (105) as well as with a theoretical prediction made by Longuet-Higgins (147).

The electrical properties of hexaborides have also been studied by Lafferty (105). Considerable attention was devoted to LaB_6 which, because of its low work function and high thermal stability, shows considerable promise as a thermionic electron emitter for high-temperature applications. It was found that when the material is heated to a sufficiently high temperature, metal atoms at the surface begin to vaporize. Because of the strength of the metal-boron bonds, the rate of vaporization is low; Lafferty's measurements indicate that the latent heat of vaporization of lanthanum from lanthanum boride equals 169 Kcal. per mole, an unusually high value. The metal atoms which are vaporized are rapidly replaced by diffusion from the bulk. At this stage, no appreciable vaporization of boron atoms occurs and the boron framework remains intact. Unlike oxides and other ionic compounds, the LaB_6 structure is stable over a wide range of composition; as many as one-fourth of the metal atoms may be lost without causing the collapse of the structure.

46a.

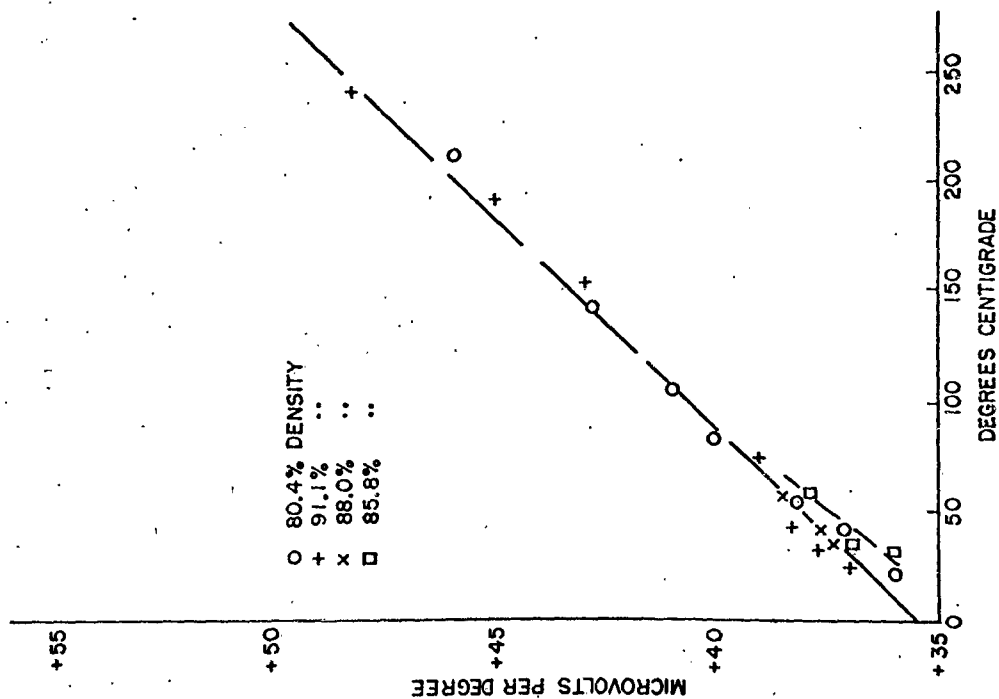


Fig. 14. Thermoelectric power of sintered TiP_2 vs. Constantan. ($d\theta/dT$ vs. T)

46b.

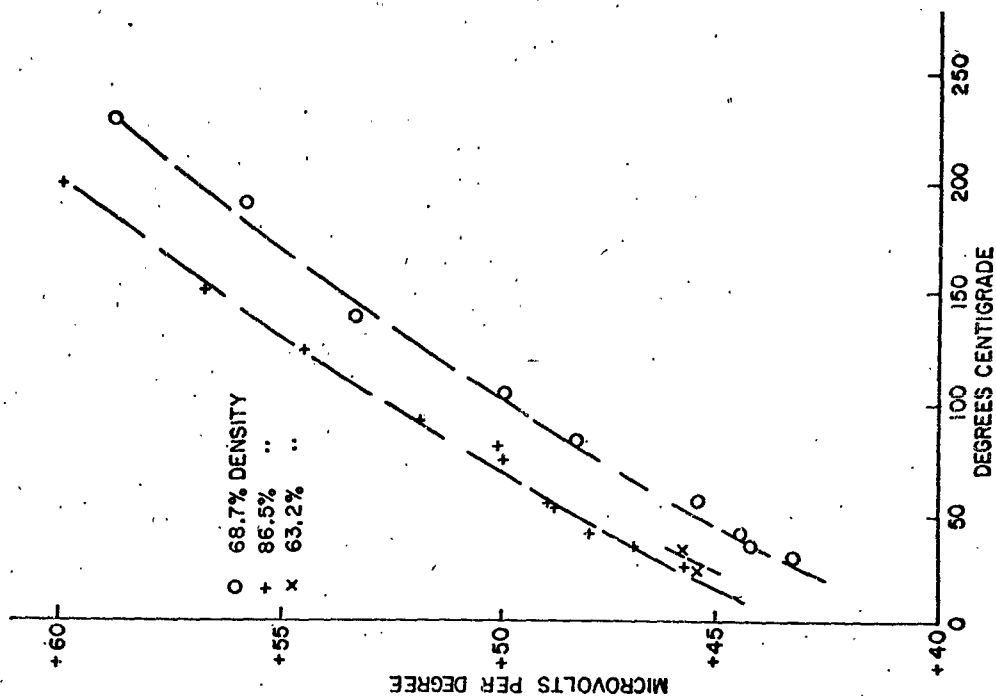


Fig. 15. Thermoelectric power of sintered Vb_2 vs. Constantan. ($d\theta/dT$ vs. T)

TABLE XIV: Electrical Properties of Hexaborides (Ref: 139)

Metal	Resist-ivity microhm cm.	Hall Coeff. $R \times 10^4$ cc/coul.	Thermal e. m. f. microvolt/deg.	Mobility of carriers $\text{cm}^2/\text{volt. sec.}$	Number of cond. electrons per metal atom	Thermal Coeff. of elect. res. $\times 10^3/\text{degree}$ (0 - 100°C)	Work Function (Electron volts) References:	
						124	122	105
Ca	222	-91.0	-32.8	+41.0	0.05	+1.16	---	2.86
Sr	111	-76.3	-30.3	68.7	0.06	+ .83	---	2.67
Ba	77	-57.5	-26.2	74.7	0.08	+1.08	---	3.45
Y	40	-4.6	-0.5	11.4	0.96	+1.24	---	---
La	15*	-5.0	+0.1	33.1	0.90	+2.66	2.22	---
Ce	20	-8.2	+0.3	14.2	1.06	+1.00	2.66	2.66
Pr	20	-4.3	-0.6	22.2	1.02	+1.92	2.59	2.59
Nd	20	-4.3	+0.4	22.0	1.00	+1.93	3.97	---
Sm	207	+1.5	+7.6	0.74	2.86	-0.42	3.46	---
Eu	85	-50.2	-17.7	59.3	0.09	+0.90	4.4	---
Gd	45	-4.4	+0.1	9.8	0.94	+1.40	---	---
Tb	37	-4.6	-1.1	12.2	0.94	+1.31	---	---
Yb	47	-83.6	-25.5	179.4	0.05	+2.34	3.1	---
Th	15	-2.2	-0.6	14.7	1.99	+2.31	---	2.92

* Obtained by extrapolation to zero porosity (121).
Lafferty (105) reported 27 microhm.cm.

As a result, the LaB_6 surface retains its activity and remains essentially unchanged throughout the heating process and does not show the rapid deterioration characteristic of metal and oxide surfaces under comparable conditions.

Diffusion of metal atoms to the surface continues until the hexaboride structure collapses and is replaced by that of pure boron. It is clear that, if Lafferty's picture is correct, the final melting point must be that of pure boron. Lafferty found that the melting points of the hexaborides of Ca, Sr, Ba, La, Ce and Th, all lie within the range $2230 \pm 40^\circ\text{C}$ (Lafferty's measurements). This was interpreted as implying that in all these cases the recorded melting point was that of essentially pure boron.

The electrical resistivity of LaB_6 varies from about 25 microhm-cm. at 20°C to 120 microhm-cm. at 1600°C (105). Paderno, et al. (121) reported similar results; they found that the resistivity changes from 18 microhm-cm. at room temperature to 140 microhm-cm. at 2000°C . Over this range the thermal coefficient of resistivity is 0.06 microhm-cm/deg.; the comparable coefficient for metallic lanthanum is 0.218 microhm-cm./deg.

F. Bonding:

It is convenient to classify the many theories of interatomic bonding in refractory borides in terms of the types of electron transfer assumed to take place when the bond is formed. Kieseling (1f), Juretschke and Steinitz (136) and others consider that the formation of these bonds is accompanied by the transfer of electrons from the boron to the metal atoms. Opposed to this is the view expressed variously by Pauling (150), Longuet-Higgins and Roberts (147, 148), Lipscomb (143) and Samsonov (137, 139) to the effect that the bonding process involves the transfer of electrons from the metal to the boron atoms.

The latter position appeals strongly to those who look upon the formation of a boride primarily as a chemical process, and who interpret interatomic bonding in terms of ionization potentials, relative electro-negativities and bonding orbitals with calculable electron requirements.

This point of view has been adopted by Johnson and Isaacs (147) who studied phase relationships in the lanthanum-boron system and examined critically the available electrical and magnetic data for LaB_6 . The great hardness and the high melting point of that compound were cited in support of the view that its outstanding structural feature is the strong and relatively rigid boron network.

They found that the lanthanum hexaboride phase is stable from $\text{LaB}_{7.8}$ (it is probably more useful to refer to the latter as $\text{La}_{0.76}\text{B}_6$). This wide range of homogeneity was explained in terms of the electron requirements of the boron network and the availability of such electrons in the valence band of the metal atom. Calculations by Longuet-Higgins and Roberts (148) and by Lipscomb and Britton (143) indicate that two electrons must be transferred to each boron octahedron in the hexaboride structure to ensure its stability. In stoichiometric LaB_6 there is therefore one "excess" valence electron for each lanthanum atom. Lafferty (105) has actually interpreted his Hall constant measurements in terms of the presence of one such negative current carrier for each lanthanum atom in (presumably stoichiometric) LaB_6 . From this point of view a deficiency of metal atoms can be tolerated, so long as enough electrons are made available to the boron network. A lower limit of $\text{La}_{0.67}\text{B}_6$ is theoretically possible, with each lanthanum atom contributing all three valence electrons to the boron net; at that composition the phase would presumably be an electrical insulator. Actually, the observed lower limit occurs at $\text{La}_{0.76}\text{B}_6$, a limit which may be determined by the onset of mechanical instability in the boron lattice due to the large number of metal atom vacancies.

The authors have utilized similar considerations to explain the variation of the lattice constants of EuB_6 with composition. In this phase, which also has a wide range of homogeneity, all the Eu atoms would be expected to be in the +2 state at the stoichiometric composition, at which point the lattice constant should be a maximum (See Fig. 9). As the relative amount of Eu is decreased (i.e., in the presence of a relative excess of boron), the electron requirements of the boron network can be satisfied only by the conversion of Eu atoms from the +2 to the +3

state. In the latter state the effective size of the metal atom is decreased, resulting in the observed decrease in the lattice constant.

Samsonov and co-workers (50, 104, 137) have for some time emphasized the importance of low values of the first and second ionization potentials of the metal atom for the formation of stable binary borides. It is assumed that electron transfer takes place from the relatively electropositive metal atoms to the electron-poor boron atoms. Meshor and Samsonov (50) postulate that in the hexaborides each metal atom must transfer two electrons to the boron network.

Their empirical analysis of the ionization potentials of the metals indicates that such transfer is unlikely to occur if the first ionization potential of the metal exceeds 6.6 to 6.8 electron volts, or if the second exceeds 11.5 to 12 electron volts. The failure of metals like Ga, In, Tl, Ge, Sn and Pb to form borides is ascribed to the high ionization potentials of these metals and their consequent inability to transfer electrons to the boron lattice (130). Vacancies in an inner electron shell are also stressed as a necessary condition for the formation of borides. It is pointed out that there are no alkali metal borides nor any borides of B subgroup metals. It is difficult, however, to reconcile this argument with the acknowledged stability of alkaline-earth and aluminum borides or with the existence of gold and silver diborides. In none of these metals (i.e., alkaline earths, aluminum, gold and silver) are there unfilled inner electron shells, and in the case of both gold and silver the ionization potentials exceed by a large margin the limits mentioned by Meshor and Samsonov.

Longuet-Higgins and Roberts have used the method of localized molecular orbitals to determine the electron requirements of boron icosahedra in boron carbide (147) and of boron octahedra in the hexaborides (148). Both types of boron networks were found to be electron deficient, requiring electrons from outside sources for stability.

Lipscomb and Britton (143) extended this work and have outlined a valence theory of the structures of the higher borides. It is assumed that the boron framework may be isolated into polyhedra connected by localized bonds. The molecular orbitals of individual polyhedra are then investigated, and the electron requirements for bonding in these polyhedra are considered to be satisfied by transferring electrons from the relatively electropositive metals to the boron framework until the bonding orbitals of the latter are filled. Excess metal valence electrons, if any, are responsible for the observed metallic properties.

Lipscomb and Britton have computed the bonding requirements of the groups of twelve boron atoms arranged at the vertices of cubo-octahedra in MeB_{12} ; the method used is similar to that used by Longuet-Higgins and Roberts for boron icosahedra (147). In the cubo-octahedra of the dodecaborides each boron atom forms four internal and one external bond to other boron atoms. An LCAO molecular orbital approach indicates that thirteen internal electron pair bonds are formed by each group of twelve boron atoms. The latter can furnish thirty-six valence electrons but, of these, only twenty-four are available for internal bonds. Twelve additional valence electrons are needed for the twelve external bonds. There is an overall deficiency of two electrons and these are furnished by the metal atom. If the metal were divalent the dodecaboride would be an insulator, or at best a poor conductor. In ZrB_{12} the metal atom has four valence electrons and the compound is metallic; considerations of this sort may be used to account for metallic properties in the rare-earth dodecaborides.

Similar calculations indicate that each B_6 octahedral group in MeB_6 needs twenty electrons to satisfy its bonding requirements (fourteen for seven internal orbitals and six more for six external bonds). The six boron atoms can furnish only eighteen and the deficiency is made up by the metal. In this basis it would be expected that the alkaline-earth hexaborides would be insulators. Although

precise data for highly purified specimens are not available, the data in Table XIV do indicate that CaB_6 has the highest resistivity of all the hexaborides with SrB_6 and BaB_6 not far behind.

These modified molecular orbital techniques have also been applied to the tetraborides and the diborides. On the basis of Lipscomb and Britton's calculations the former require fifty-six electrons for the boron-boron bonds in each unit cell. The sixteen boron atoms can only furnish forty-eight; the metal atoms contribute eight (two each).

The treatment of the diborides is based on M_2B_2 as a closed shell prototype of the transition-metal diborides. Magnesium is assumed to form a doubly charged positive ion within the boron framework; the transfer of two electrons to the boron atoms makes them isoelectronic with graphite. The excess valence electrons of the transition metals account for their metallic properties.

This approach, as the authors emphasize, is far from complete in its present form. It is oversimplified and arbitrary in its description of "isolated" boron polyhedra, but it does appear to represent the beginnings of a unified picture of bonding in these borides. It does not, however, account for the inability of most Group-B metals to form borides; it ignores the presence or absence of unfilled inner orbitals in the metal atoms; and it does not account for observed trends in the electrical, magnetic and other properties of the di- and hexaborides.

The alternative picture of the bonding process in borides, i.e. that in which electron transfer is assumed to proceed from the boron to the metal lattice, has been presented clearly and persuasively by Klossing (1f). In discussing borides as interstitial phases, evidence based on crystal structure analyses and magnetic measurements is brought forth in support of the view that the interstitial boron atoms act as electron donors; in the diboride, the electrons are believed to be taken up by the incomplete d shells of the transition-metal atoms. Juretschke and Steinitz (136) have taken a similar position. Their simple model (See Section IV, D) in which it is assumed that the three valence electrons of each boron atom

participate in the occupation of metal d bands, accounts satisfactorily for the electrical resistivity and Hall constants of various transition-metal diborides.

These explanations have been limited thus far to the transition-metal diborides. They are far from satisfactory in their present form, despite their successful application to the interpretation of electrical and magnetic measurements. For example, it is difficult to reconcile the assumed transfer of three electrons from each boron atom to the metallic bands with the known relative electronegativities of the two types of atoms. It is also difficult to accept the statement of Juretschke and Steinitz that "the principal role of the boron atoms is the stabilization of a simple hexagonal metallic structure without any pronounced boron to boron bonds". A careful analysis of the lattice constants of the diborides and the higher borides indicates, to the present author at least, that the iron networks play a very important part in these structures and that boron to boron bonds must be extremely strong. Admittedly, the model proposed by Juretschke and Steinitz is a first approximation; a more refined treatment of the problem would necessarily have to take the boron bands into consideration, and in so doing may avoid some of the difficulties of the simpler treatment.

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